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(Limestone Injection Multistage Burner) Burner

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KINETIC STUDIES RELATED TO THE LIMB BURNER

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16. ABSTRACT The report gives results of theoretical and experimental studies of subjects related to the limestone injection multistage burner (LIMB). The main findings include data on the rate of evolution of H ₂ S from different coals and on the dependence of the rate of evolution on the distribution of organic sulfur functionalities in the coal. A method was developed for determining the pore structure of solids at high temperatures which also allows estimates of the diffusion and adsorption coefficient of the gases onto the solid surface using the pulse dispersion method (PDM) and Fourier analysis. The method was applied to the sintering of lime. In addition, the PDM was used to determine the influence of sulfation on the diffusion of gases into lime. Several other studies were conducted, including analyzing the influence of ash composition on ash fusion temperature and developing new correlations for their estimate. The surface forces on coal and how they affect the adherence of minerals to the surface were determined. Also, the rates of reduction of iron pyrite and doped iron pyrite by hydrogen were measured. A comprehensive survey of the chemistry and kinetics of the various reactions which occur in LIMB is presented, along with new findings.		
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REPORT STRUCTURE

This report covers the work done at NCSU during the period February-May 1983 on the cooperative agreement R809724. The work was conducted by several people including Mr. D. Warren, K. Lockerby, R. Reinhardt, D. Lynn, W. Sahlie, J. Potente, D. Jones, D. Donohue, B. Drews and Dr. A. Attar. The work covered several theoretical and experimental subjects, including: (1) development and testing of a method for measurements of the pore structure solids using pulse techniques, (2) preparation of well-defined samples of calcined limestone and iron-doped calcined limestones, (3) building a reactor for studies of the kinetics of gaseous evolution from rapidly heated coal particles, and testing the rate of H_2S evolution from different coals, (4) building two porosimeters for "static" pore-structure analysis, (5) preparation of a set of well-characterized coals for sulfur kinetics studies, (6) studying the kinetics of reduction of FeS_2 with H_2 , (7) fixing a pulse differential reactor and preparing it for studies of the kinetics of the reactions of H_2S with $CaCO_3$, CaO and iron-doped $CaCO_3$ and CaO , (8) building a part of a complex analytical system using a quadrupole mass-spectrometer for studies of fast reactions at high temperatures, (9) studying the rate of sintering of lime and its effect on the diffusion coefficient of gases in it, (10) studying the diffusion coefficient of gases in partially sulfated lime, (11) analyzing coal-ashes and limestones for their composition using NAA, (12) studying the oxygen functional groups in several coals and their effects on the coherence of minerals to coal surfaces, (13) conducting a broad literature survey of the reactions of sulfur-containing gases with calcium-containing minerals, (14) conducting theoretical studies on the rate of decomposition of limestone particles and (15) conducting a detailed study on the dependence of ash fusion temperatures on the ash composition and in particular on the calcium content of the ash.

The status of research on each of these subjects will be reviewed. Several issues delayed the progress of the work. One was a sequence of delays in the purchasing of a high-temperature furnace, which was received too late. Another set of difficulties arose from the lack of adequate ventilation and electrical facilities in Riddick laboratories, which forced shutting down equipment on more than one occasion.

Five papers were prepared in the project; therefore, copies of the drafts of the papers are enclosed instead of the technical introduction (Chap. 1) (accepted for publication), the reaction of H_2 with FeS_2 (Chap. 6), and the ash-fusion temperature study (Chap. 9) (accepted for publication).

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CHAPTER 1

RETENTION OF SULFUR IN COAL ASH AND IN CALCIUM CONTAINING ADDITIVES DURING COAL COMBUSTION

1.1 INTRODUCTION

It has been established that sulfur is retained in coal ash (e.g., Selvig and Gibson, 1956) and in coal-combustion additives (e.g., Stambaugh et al., 1977; Merryman and Levy, 1982). Therefore, numerous studies have recently been conducted in which coal additives were examined as means to achieve sulfur and nitrogen oxide control (Attar, 1978a); Freud and Lyon, 1980; Case et al., 1982).

Sulfur is retained in coal ash in two main forms: as physically adsorbed SO_2 , predominantly on iron oxides and as chemically bound sulfur (Baker and Attar, 1981). The chemically bound sulfur is predominantly calcium sulfate, although some sulfides have also been found in ashes where incomplete combustion of the coal occurred (Attar, 1978).

In this paper, the chemistry, the thermodynamics and the kinetics of the various reactions that influence trapping and retention of sulfur in coal ash and in calcium-containing additives are reviewed and some new data are presented.

1.2 THE BASIC MECHANISM OF COAL COMBUSTION: QUALITATIVE OBSERVATIONS

Coal combustion is viewed almost universally as a two-step process:

1. A rapid pyrolysis step which produces char and volatiles. The volatiles are also partially oxidized at this step.
2. A relatively slower combustion process in which char is burned to carbon dioxide and ash.

Regardless of whether the AVERAGE environment in the combustor is oxidizing or reducing, during the pyrolytic stage, the LOCAL

environment around each particle is reducing. However, during the burning of the char, the local environment around each particle is much more oxidizing. The latter reaction is an exothermic process, with a rate which is either reaction controlled or diffusion controlled. Several reviews of the kinetics and mechanism of coal and char combustion have been published, e.g., Sherman and Landry (1963), Mulcahy and Smith, and Smoot and Pratt (1979).

The yield and rate of the pyrolysis step depends predominantly on the type of coal burned, on the heating rate, on the oxidizing environment and on the coal particle size. Therefore, the difference in the rate of volatilization of a particular coal in different burners depends predominantly on the heating rate that the coal particles achieve in these burners. Obviously, different rates of volatilization are achieved in fluidized beds (FBB), stokers, and pulverized fuel burners (PFB). Once the initial volatilization of the coal particles is complete, the char produced begins to burn. The rate of burning depends on many variables but the most important one is the temperature. Most studies are consistent with the thesis that the rate of low-temperature combustion, i.e., at temperatures below, say, 1200°C or so, is controlled by the rate of the chemical reaction while the rate of high-temperature combustion is controlled by the rate of mass transfer of the oxidants O_2 and CO_2 into the porous char particles (Mulcahy and Smith, 1969).

Volatilization occurs in the temperature range 400-850°C and residence time of 0.001 sec to 5 min. Burning of char occurs in the temperature range 1200-2000°C and 0.001 to 5 min, in pulverized fuel combustors (PFC) and 790-930°C, 5 min to 2 hours in FBC. The tremendous difference among different burners in the conditions in the char-combustion zone implies that different reaction kinetics prevail in each case.

A large body of data has been obtained on the rates and the mechanisms of the reactions of sulfur-containing compounds with calcium-based materials. The majority of these data were obtained in the temperature range 400-900°C and residence times of the order of 10 min to 30 hours. Since pulverized coal and many other combustion operations

are conducted in the range 1200-2000°C and with residence times of the order of 0.01 sec-5 min and because very little data are available on the chemistry, kinetics and mass transport which influence the trapping of sulfur in these conditions, such data need to be obtained.

1.3 ON THE MECHANISM AND KINETICS OF THE FORMATION OF SULFUR-CONTAINING GASES AND THE RETENTION OF SULFUR ON CALCIUM-BASED MINERALS

Coal burners are gas-solid reactors. Four reaction subsystems influence the sulfur: 1) the solid coal; b) the iron pyrite; c) the calcium-containing natural minerals and additives; and d) the gas phase. The reactions that occur in each phase influence the final result: the fraction of sulfur retained in the solid and the fraction remaining in the gas. The various reactions that take place will be discussed in accord with the stage in which they occur, i.e., the volatilization stage and the char combustion stage.

1.3.1 Chemistry and Kinetics of the Reactions of the Coal Sulfur in the Volatilization Step

The main reactions that occur in the volatilization stage and influence the retention of sulfur in the ash are summarized in Table 1.1. Most of the information in the table was taken from a review by Attar (1978).

1.3.2 Chemistry and Kinetics of the Reactions in the Char-Oxidation Stage

In the early part of the char-oxidation step, the local environment around the char particles is still reducing and contains, among other gases, carbon monoxide. The remaining sulfur at this stage is bound as FeS, CaS, and as "organic" sulfur. The author of this manuscript believes that even in the "oxidizing zone," since the main gases inside the char particle are CO and CO₂, the sulfur compound volatilized is COS. The reactions

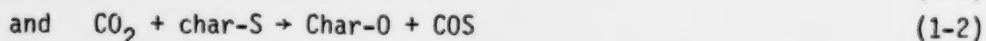
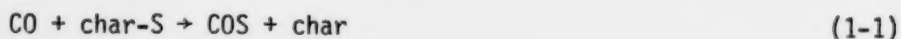


TABLE 1.1 TRANSFORMATION RELATED TO THE ROLE OF THE SULFUR
IN THE VOLATILIZATION STAGE

Reaction	Kinetic Information	References
<u>Reaction Associated with the Solid Coal</u>		
1. $RSH \rightarrow HC + H_2S$ Decomposition of thiolic functional groups	Is complete in $t < 25$ min when $T \sim 350^\circ C$.	Attar et al. (1980) and Attar et al. (1983)
2. $RSR' \rightarrow HC + H_2S$ Decomposition of sulfidic functional groups	Fast $T \sim 450^\circ C$	Attar et al. (1980) and Attar et al. (1983)
3. $FeS_2 + Coal \rightarrow HC + FeS + H_2S$	$T > 550^\circ C$ fast	Many references cited by Attar (1978), Attar et al. (1976)
4. $Coal \rightarrow Char + gases + thiophenes and tar$ Decomposition of the coal organic matrix and release of thiophenes	$T > 450^\circ C$ fast	

are likely the reactions that volatilize the sulfur. The COS formed may be oxidized subsequently to SO_2 and CO_2 . As the oxidation process proceeds, the intraparticle environment becomes more and more oxidizing: the calcium sulfide is oxidized to the sulfate. Table 1.2 summarizes much of the available information on these reactions.

1.4 BASIC MINERALS IN COAL AND THEIR DECOMPOSITION DURING COMBUSTION

The most important basic minerals in coal are calcium, magnesium, and iron-based carbonates, although small amounts of sodium and potassium-containing minerals can also be found (Gluskoter et al., 1981).

Calcium is present as the minerals calcite (CaCO_3) and dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) (Gluskoter and Rao, 1973; Ward, 1977). Ankerite, a carbonate containing iron, calcium and magnesium, was found in British coals by Dixon et al. (1970). Ion-exchanged calcium was also found in coals, predominantly in lignites and subbituminous coals (Given et al., 1979). Iron carbonate, siderite (FeCO_3), was found in Australian coals (Kemezys and Taylor, 1964; and Smyth, 1966).

When coal is injected into a combustor, the carbonates heat and either decompose to the oxides or react with acidic gases. The main reactions that occur in the reducing and in the oxidizing zones which involve calcium are listed in Table 1.3. Caldwell et al. (1977) established that the rate of decomposition of calcium carbonate depends on the gaseous environment around the particles, and therefore is probably limited by the rate of heat transfer achievable at the specific type of operation. Dubil (1977) solved the differential equations describing the thermal decomposition of solids limited by the rate of heat transfer.

For calcium carbonate particles smaller than 250 microns, lumped temperature and concentration formulations may give a 0-order approximation for predicting the limestone particle status in the combustor. The main assumptions used in the formulation are that: 1) the particle temperature is uniform at any instant, 2) the particle maintains its physical integrity during the decomposition, 3) heat exchange occurs by conduction, convection and by radiation. The conduction and convection

TABLE 1.2 REACTIONS OF SULFUR SPECIES IN THE CHAR OXIDATION STAGE

Reaction	Kinetic Information	References
1. Bound Sulfur + $O_2 \rightarrow SO_2 + SO_3$ Gasification of the sulfur.	No kinetic data are available	Attar (1978)
2. $CaS + O_2 \rightarrow CaSO_4$ Oxidation of calcium sulfide to calcium sulfate.	No data are available	
3. $FeS_x + O_2 \rightarrow FeSO_4$ Oxidation of iron sulfide to iron sulfate	Depends strongly on the preparation of the FeS . FeS can be pyrophoric.	Attar (1978b)
4. $FeSO_4 \rightarrow FeO + SO_3$ Decomposition of iron sulfate.	Complete at $T \ 490^\circ C$	Attar (1979a)

TABLE 1.3 REACTIONS ASSOCIATED WITH THE LIMESTONE OR DOLOMITE

Reaction	Kinetic Information	References
1. $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ Limestone decomposition to porous CaO and CO_2	Fast at $T > 750^\circ\text{C}$ in inert atmosphere or vacuum. Avrami-Erofeev equation (see ref. Jacobs (1968)) describes kinetics best. Heat and mass transport influence the apparent rate of decomposition.	Hills (1968) Gallagher and Johnson (1973) and (1976) Searcy and Beruto and Jacobson, Robert and Searcy (1978)
2. $\text{CaCO}_3 \cdot \text{MgCO}_3 \rightarrow \text{CaO} \cdot \text{MgO}(\text{CO}_2)_x + \text{CO}_2$ Partial or complete decomposition of dolomite to calcium and magnesium oxides	Fast around 800°C Can be performed reversibly and in cycles	Dobner et al. (1977), Li and Rogan (1978), Powell and Searcy (1978)
3. CaO (porous) $\rightarrow \text{CaO}$ (No-porous) Sintering and elimination of pores accessible to the gas molecules	Occurs with timescale of 20-60 min when $T > 1250^\circ\text{C}$	Attar (1979) Staley and Greenfeld (1949)

terms can be lumped into a single term as described by Aylin and Smith (1974), 4) the emissivity of the particle is a constant, 5) the kinetics of the decomposition follows that described by Gallagher and Johnson (1973). For a spherical particle:

$$m_o[(1-\alpha)C_{p1} + \alpha C_{p2}] \frac{dT}{dt} = Ah(T_1 - T) - k_o m_o (1-\alpha) \Delta H_R e^{-\frac{E}{RT}} + A \epsilon_o (T_1^4 - T^4) \quad (1-3)$$

$$\frac{d\alpha}{dt} = 2k_o (1 - k_o t e^{-\frac{E}{RT}}) e^{-\frac{E}{RT}} \quad (1-4)$$

For most practical purposes, the decomposition is complete before the particle temperature reaches 1100°C; therefore, for pulverized coal burners, where $T_1 \sim 1500-2000K$ $T_1^4 \gg T^4$. For fluidized bed burners the radiation term is negligible altogether. The magnitude of the heat transfer coefficient, h , depends on the flow field and can be obtained from correlations or approximated by the equation:

$$h = \frac{k_g}{r} \quad (1-5)$$

or by (Aylin and Smith, 1974):

$$h = \frac{5.83 \cdot 10^{-5}}{r} \left(\frac{T + T_1}{4.273} \right)^{1.64} \quad (1-6)$$

Alternatively, one may use the equation (Babily, 1974):

$$\frac{2hr}{k_g} = 2 + 0.17 \left(\frac{2rV \rho g}{\mu} \right)^{0.66} \quad (1-7)$$

where h is in cal/cm·sec°K and T and T_1 in °K. The particle size does not change much in the decomposition; thus, $r^2 \approx r_o^2$. Equation (1-3) can therefore be simplified to the form:

$$((1-\alpha)C_{p1} + \alpha C_{p2}) \frac{dT}{dt} = \frac{Ah}{\rho V_o} (T_1 - T) - k_o \Delta H_R (1-\alpha) e^{-\frac{E}{RT}} + \frac{A}{\rho V_o} \epsilon_o \sigma (T_1^4 - T^4) \quad (1-8)$$

Note that in the general case T_1 is not a constant and will depend on the rate of heat evolution on the limestone particle trajectory. However, for FBC, T_1 often can be taken as a constant. The recommended values of the specific variables are $\epsilon_o = 0.08$, $E = 145$ kcal/mole, $k_o = 5.10^{27} \text{ sec}^{-1}$, $C_{p1} = 20.13 + 10.24 \cdot 10^{-3} T - 3.34 \cdot 10^{-2} T^2$ and $C_{p2} = 11.67 + 1.08 \cdot$

$10^{-3} T - 1.56 \cdot 10^{-5} T^2$; $\rho = 0.02973 \text{ mole/cm}^3$ and $\Delta H_R = 43,748 \text{ cal/mole}$. Note that the reaction is endothermic and thus initially the particle does not heat up very rapidly until it is completely decomposed. Figures 1-1 and 1-2 (Attar, 1982) illustrate the temperature-time program and the conversion-time program that limestone particles of 5 and 30 microns go through in combustion chambers at different temperatures. Since the decomposition is endothermic and its kinetics depends very strongly on the temperature, most of the decomposition occurs around 1250°K. However, since the rate of heating is different at different combustor temperatures, up to an order of magnitude of variability in the decomposition time may be observed for the same size particles. This implies that limestone particles may escape from the reducing zone not fully decomposed, depending on the temperature. Longer time is of course needed to decompose larger particles at the same chamber temperature. Therefore, larger limestone particles are more likely to escape the reducing zone undecomposed and to trap sulfur in the oxidizing zone. This is undesirable, as will be discussed later. Figures 1-3 and 1-4 show particle temperature-time program, and the conversion-time program for different size particles at 1473°K and 1873°K temperatures.

Once the limestone particle decomposes, it begins to sinter and shrink while it is reacting with H_2S in the reducing zone and/or with the SO_2 and O_2 in the oxidizing zone.

Borgwardt et al. (1971) correlated the surface area of calcined limestone with the calcination temperature. His data suggest that the specific surface area depends on the temperature and the residence time in the reactor, as was shown by Staley and Greenfeld (1949) and by Fischer (1955).

Another important variable which influences the pore structure of calcined calcite and of half-calcined dolomite is the chemical composition of the gaseous environment at the time of calcination. Kearns et al. (1978) proved that calcining limestone in a CO_2 -rich environment results in a solid with an increased ratio of large pores (>0.1 microns)

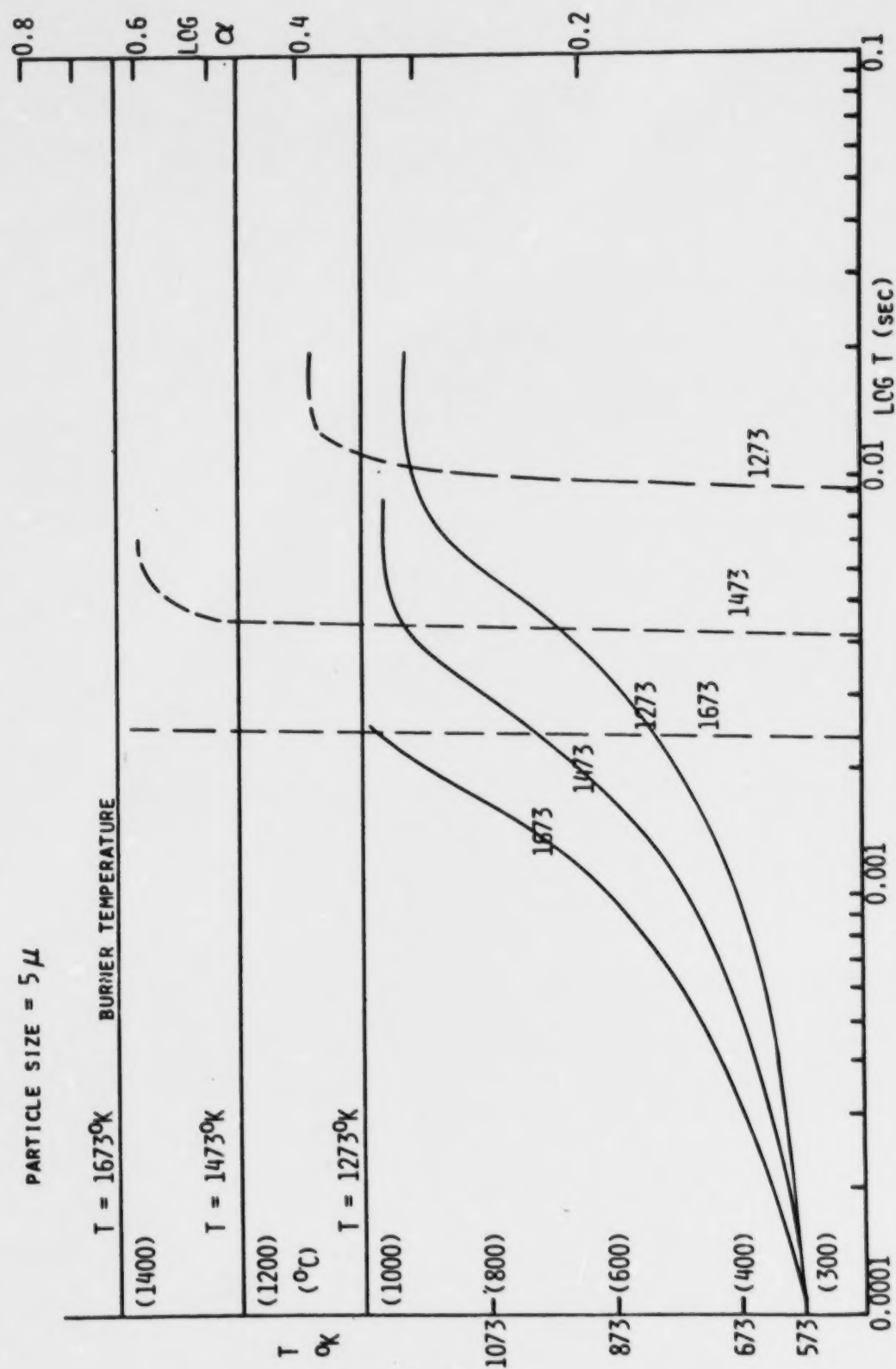


Figure 1.1 Temperature and conversion of 5-micron limestone particle vs. time injected to combustors at different temperatures

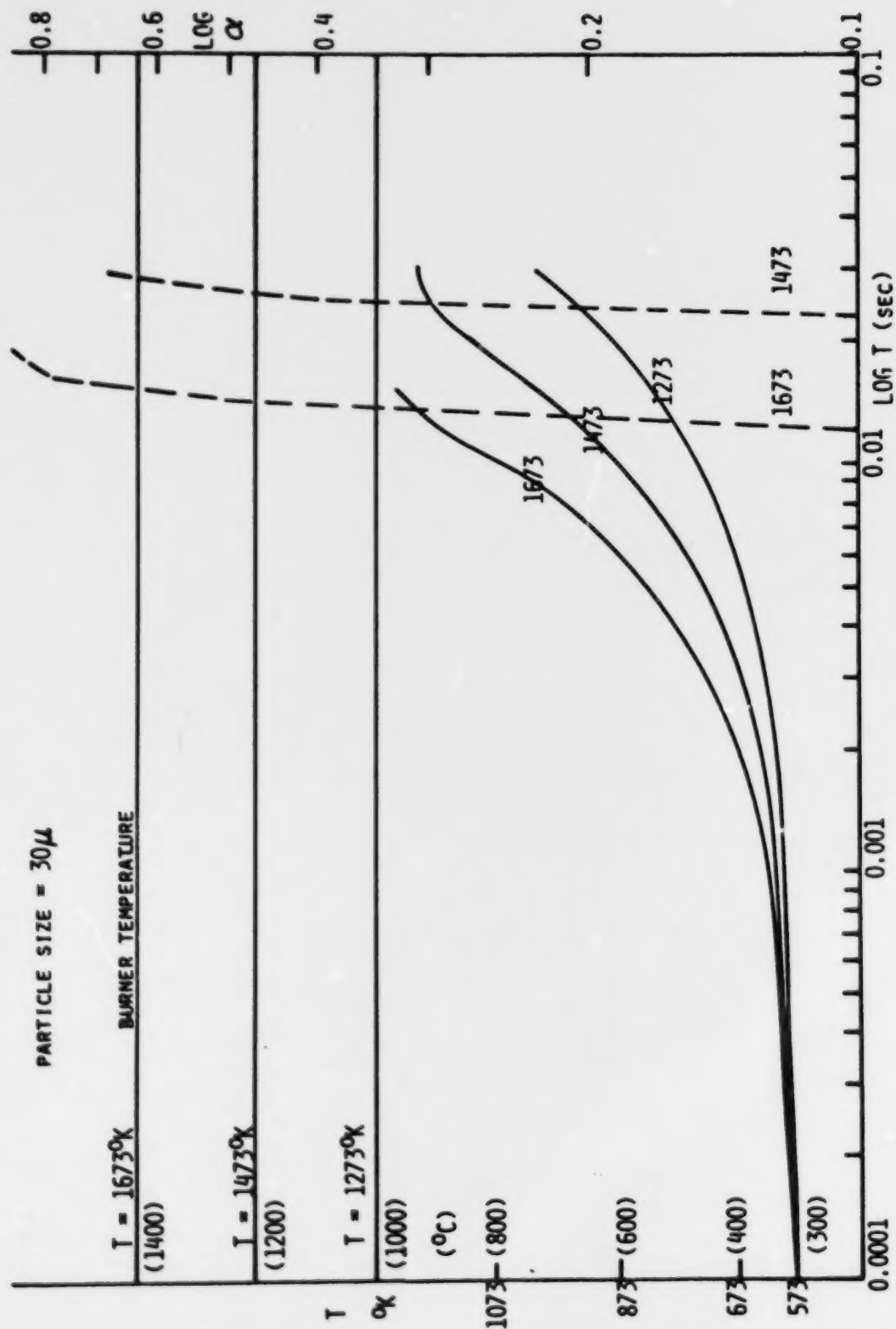


Fig. 1.2 Temperature and conversion of a 30-micron limestone particle vs. time injected to combustors at different temperatures

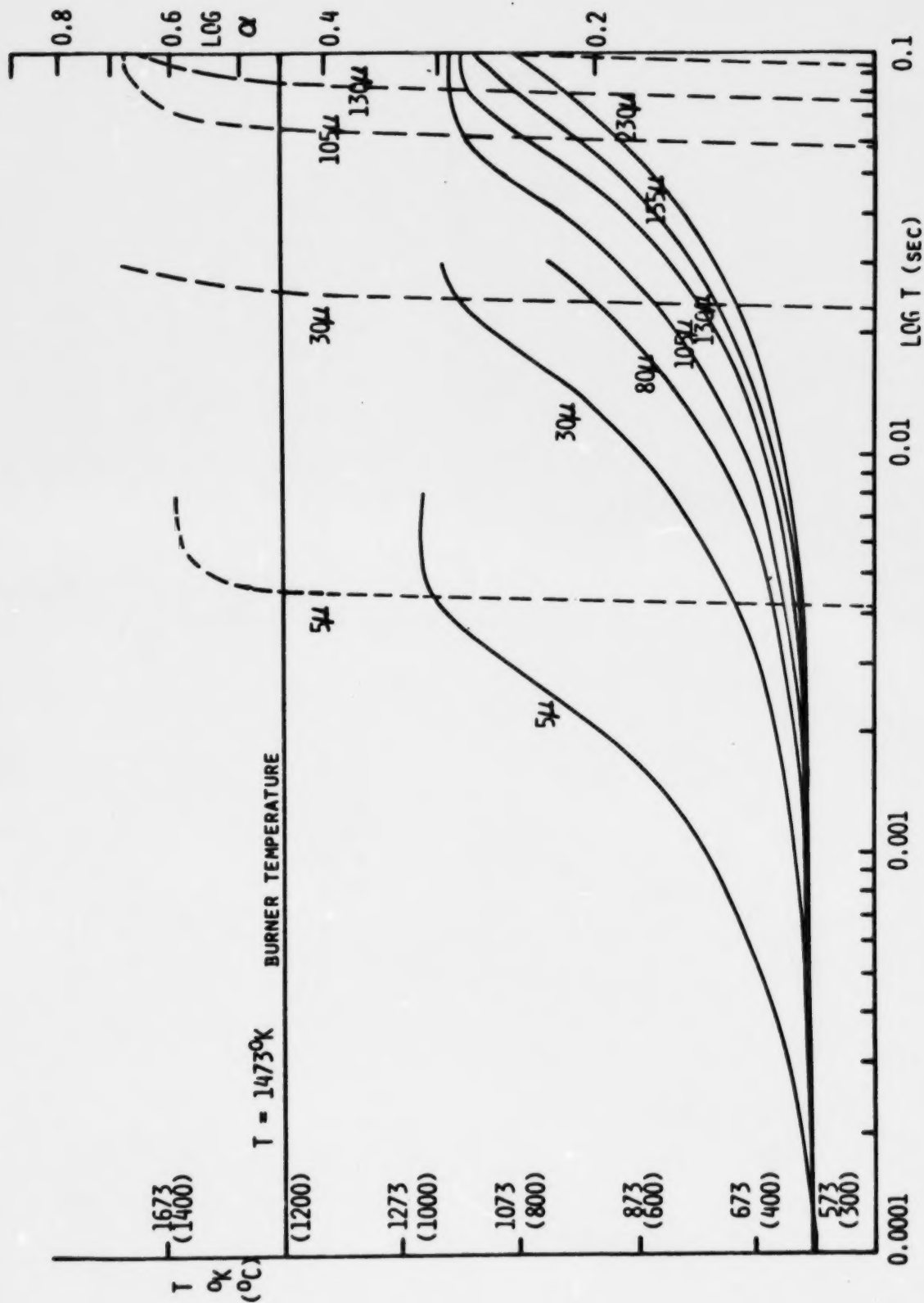


Figure 1.3 Temperature and conversion of different sizes of limestone particles injected to a combustion chamber at 1400°C

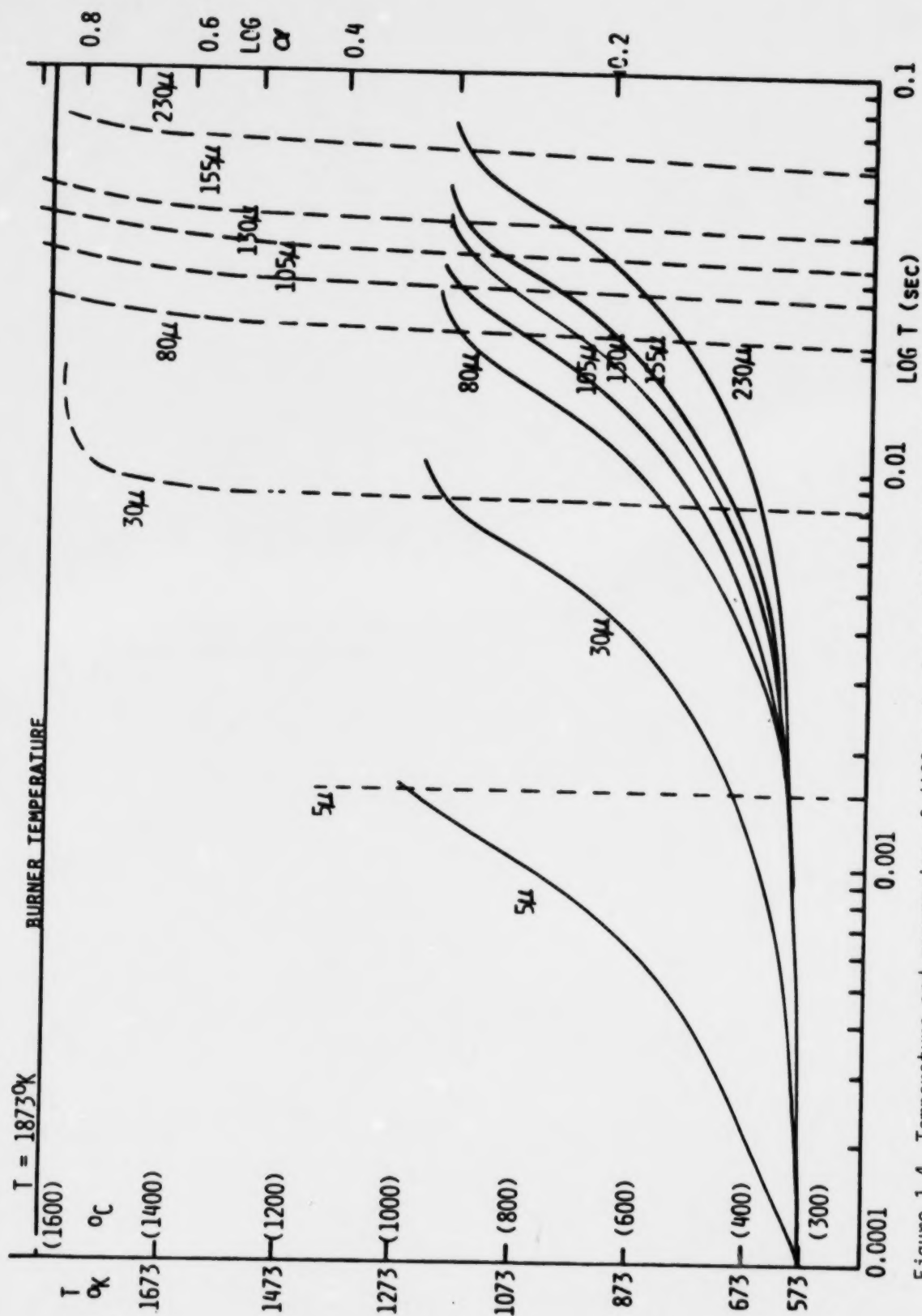


Figure 1.4 Temperature and conversion of different sizes of limestone particles injected to a combustion chamber at 1600°C

to small pores (<0.1 microns). The same phenomenon was observed by Siegel et al. (1978), who calcined dolomite in CO_2 and H_2O ; calcining limestone in a mixture of steam and nitrogen also appears to influence the pore structure of the calcine in the same manner.

Dolomite and siderite react in the burner in more or less a similar manner as calcite or limestone. However, dolomite decomposes somewhat faster than calcite (Powell and Searcy, 1978) and the decomposition of siderite is almost complete at 490°C in less than a few minutes (Attar and Dupuis, 1979). The calcium oxide formed in the decomposition of dolomite will trap sulfur in an analogous manner to CaO formed from the decomposition of calcite (Squires, 1972).

1.5 REACTIONS OF SULFUR-CONTAINING GASES WITH CALCIUM-CONTAINING MINERALS--REDUCING ZONE

The reactions which can occur between calcium-containing minerals and hydrogen-sulfide or sulfur-dioxide are described in Table 1.4. In the reducing zone the dominant sulfur-containing species are H_2S and COS , which are products of coal pyrolysis and of secondary gas-phase reactions.

The molar volumes of CaCO_3 , CaO and CaS are respectively $34.16 \text{ cm}^3/\text{mole}$, $16.49 \text{ cm}^3/\text{mole}$ and $28.86 \text{ cm}^3/\text{mole}$ (at 25°C). Therefore, when a calcite particle decomposes, a very porous lime particle is formed, theoretically with a porosity of 0.52. However, the particles shrink somewhat and often a smaller porosity is found. When the CaO reacts to form CaS , the pore mouths are narrowed since the molar volume of CaS is larger than that of CaO . Thus, in principle, CaO particles may be obtained with outer layers consisting of CaS . The models used to treat such systems are described below.

The exact fundamental mechanism of the reaction between H_2S and limestone is not clear but it may involve the intermediate surface complex $(\text{A H}_2\text{S})_2$ where A is an active surface site (Attar, 1982). The need to assume such a surface complex is supported by the observations of Borgwardt (1982) who found elementary sulfur when a mixture of

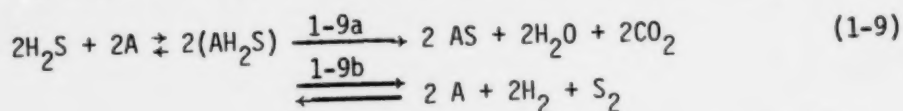
TABLE 1.4 REACTIONS INVOLVING CALCIUM-CONTAINING MINERALS AND SULFUR COMPOUNDS

Reaction	Kinetic Information	References
<u>Reducing Zone</u>		
1. $\text{CaO} + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O}$ Trapping of sulfur as CaS by reaction of H_2S with CaO.	The rate of reaction can be described by Jander's equation. $E_a \sim 37 \text{ kcal/mole}$	Attar & Dupuis (1979), Graff et al. (1972), Squires (1972), Habashi & Mikhail (1977).
2. $\text{CaCO}_3 + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O} + \text{CO}_2$ Sulfidation of limestone with H_2S .	Very limited conversion when $T < 639^\circ\text{C}$, $E_a \sim 17-19 \text{ kcal/mole}$ $T > 650^\circ\text{C}$, $E_a \sim 30-37 \text{ kcal/mole}$. Gas phase or solid-state mass transport may become controlling.	Attar and Dupuis (1979), Graff et al. (1972).
3. $\text{CaO} + \text{COS} \rightarrow \text{CaS} + \text{CO}_2$	The "grain model" with shape factor of 1.5 describes the kinetics best at 700°C .	Yang and Chen (1979)
<u>Oxidizing Zone</u>		
1. $\text{CaSO}_4 \rightarrow \text{CaO} + \text{SO}_2 + 1/2 \text{O}_2$ Decomposition of calcium sulfate	$\log P_{\text{atm}} = 8.84 - 17287/T$ $T - ^\circ\text{K}$ (equil. pressure) Fe_2O_3 catalyzes the decomposition	Lau, Cubicciotti & Hildebrand (1977), Baker & Attar (1981).
2. $\text{CaO} + \text{SO}_2 + 1/2 \text{O}_2 \rightarrow \text{CaSO}_4$ $\text{CaCO}_3 + \text{SO}_2 + 1/2 \text{O}_2 \rightarrow \text{CaSO}_4 + \text{CO}_2$ Formation of calcium sulfate	The apparent rate and capacity are limited by the pore volume of the original calcium-containing material.	Van Houte and Delmon (1979), Borgwardt (1970a, 1970b).
3. $\text{CaO} + \text{SO}_2 \rightarrow \text{CaSO}_3$ Formation of calcium sulfite.	The CaSO_3 formed tend to react with SO_2 to form CaSO_4 .	Van Houte and Delmon (1979).

TABLE 1.4 (CONTINUED)

Reaction	Kinetic Information	References
<u>Oxidizing Zone (continued)</u>		
4. $\text{CaCO}_3 + \text{SO}_2 \rightarrow \text{CaSO}_3 + \text{CO}_2$ Reaction of SO_2 with calcium carbonate.	Complex kinetics strongly coupled with the mass transport.	Coutant et al. (1970), Van Houte & Delmon (1979).
5. $\text{CaSO}_4 + 4\text{CO} \rightarrow \text{CaS} + 4\text{CO}_2$ Reduction of calcium sulfate to sulfide carbon or coal have similar effect to CO.	The layer of CaS on the CaSO_4 surface prevents further reduction of the CaSO_4 .	Wheelock & Boylan (1960), Baker & Attar (1981).
6. $\text{CaSO}_3 + 1/2 \text{O}_2 \rightarrow \text{CaSO}_4$ Oxidation of sulfite to sulfate.	The reaction is initially fast and then its rate drops. Filling of pores with CaSO_4 limits the rate.	Van Houte & Delmon (1977).
7. $\text{CaSO}_3 \rightarrow \text{CaO} + \text{SO}_2$ Decomposition of calcium sulfite.	$\log P_{\text{atm}} = 9.27 - 11710/T$ ($^{\circ}\text{K}$) (equil. pressure)	Cubiciotti et al. (1977).

5000 ppm H_2S in 70% CO_2 and the balance nitrogen and hydrogen was contacted with limestone at 750°C (Figure 1.5). Hydrogen appears to inhibit the reaction, which is consistent with the mechanism of Attar (1982).*



If it is assumed that the rate of reaction of a fresh clean surface of CaCO_3 with H_2S is controlled by the rate of the surface reaction (1-9a) and that the adsorption and desorption of H_2S and S_2 are in equilibrium, then the initial rate of reaction should depend on the partial pressures of the various species according to:

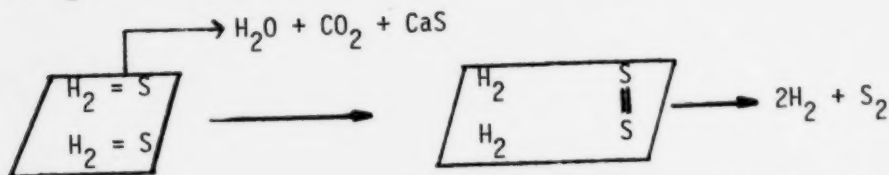
$$r_{\text{initial}} = \frac{k_f K_1 \sqrt{P_{\text{H}_2\text{S}}} + k_b K_2 K_3 P_{\text{H}_2} P_{\text{S}_2}}{(1 + k_1 P_{\text{H}_2} + K_2 P_{\text{S}_2} + K_3 \sqrt{P_{\text{H}_2\text{S}}})^2} \quad (1-10)$$

In the derivation it has been assumed that the adsorption of H_2S is dissociative. Rearrangement of the equation yields:

$$\left(\frac{k_f K_1 \sqrt{P_{\text{H}_2\text{S}}} + k_b K_2 K_3 P_{\text{H}_2} P_{\text{S}_2}}{r_{\text{initial}}} \right)^{1/2} = 1 + k_1 P_{\text{H}_2} + K_2 P_{\text{S}_2} + K_3 \sqrt{P_{\text{H}_2\text{S}}} \quad (1-11)$$

At the conditions of the experiments of Borgwardt (1982), S_2 is produced only via the decomposition of H_2S . Therefore, $P_{\text{S}_2} \ll P_{\text{H}_2\text{S}}$. When P_{H_2} is also small, one obtains:

*In the proposed mechanism H_2S is assumed to adsorb and dissociate on the dual site A. If another molecule of H_2S adsorbs on a vicinal site, H_2 and S_2 may form; otherwise, only CaS and CO_2 may form.



Thus, the relative importance of the alternative reaction paths is influenced by the density of vicinal adsorption sites on the CaCO_3 surface.

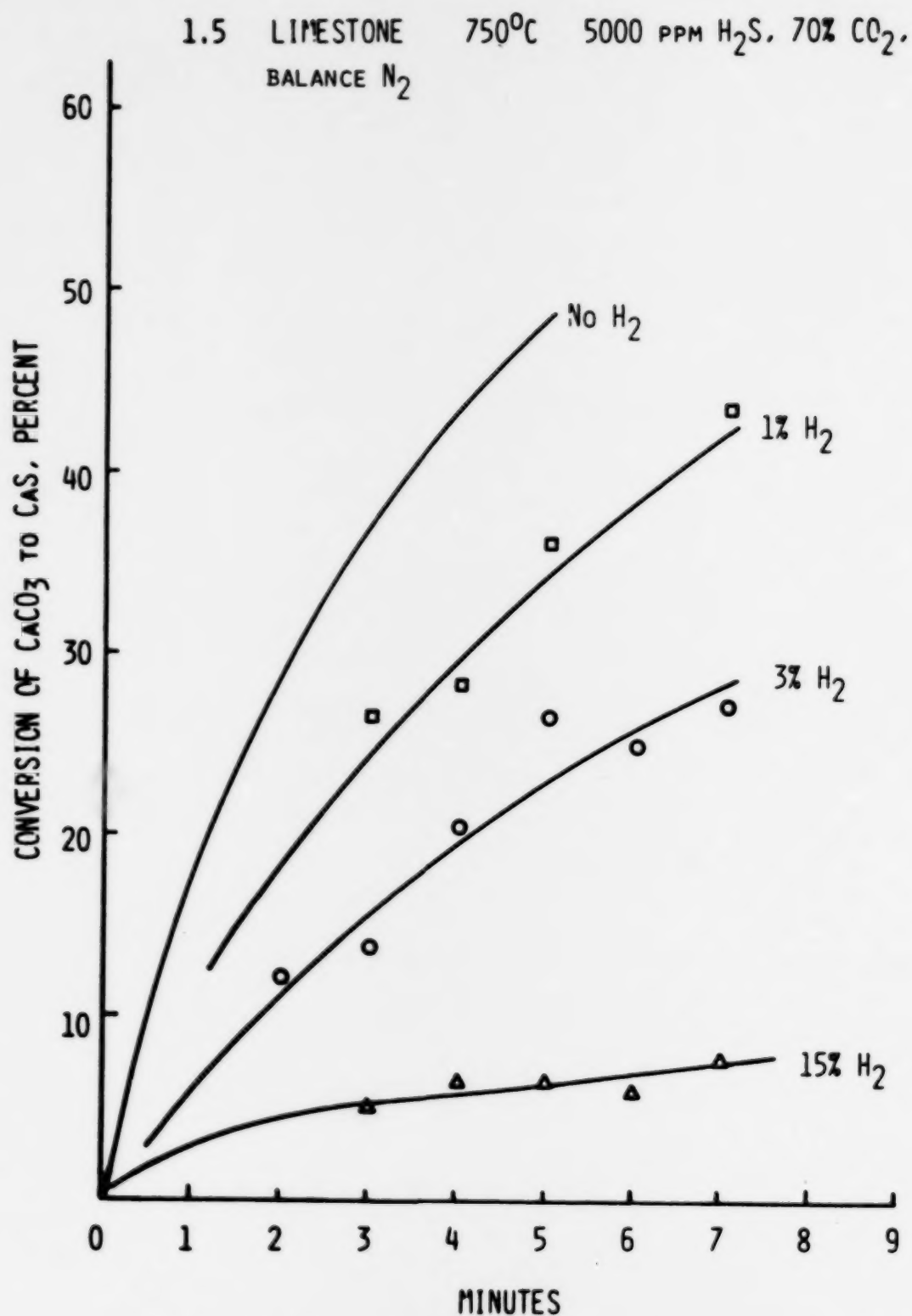


Figure 1.5 Inhibition effect of H₂ on the reaction of H₂S with limestone

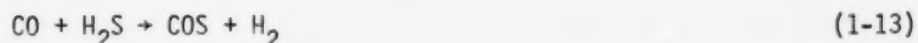
$$\left(\frac{P_{H_2S}}{r_{initial}} \right)^{1/2} \approx \frac{1}{\sqrt{k_f k_1}} [1 + K_1 P_{H_2} + K_3 P_{H_2S}] \text{Small } P_{H_2} \quad (1-12)$$

Therefore, as long as $k_f K_1 P_{H_2S} \gg k_b K_2 K_3 P_{H_2}^2 P_{S_2}$, a plot of the square root of $P_{H_2S}/r_{initial}$ vs. P_{H_2} should yield a straight line (Attar, 1982). Figure 1.6 shows the data of Borgwardt (1982) plotted in this manner. The data are consistent with the proposed mechanism and the deviation of the point at $P_{H_2} = 0.15$ atm is in the right direction, according to equation (1-12). Note that pure H_2S is still stable at temperatures below 800°C, e.g., at 727°C the equilibrium pressure of S_2 at 1 atm total pressure and 0.005 atm H_2S is approximately 0.0014 atm based on the data of Stull et al. (1969). The rate of decomposition of H_2S is, however, small as reported by Berthollet (1905). Hyne (1972) reports that at 1000°C up to 20% of the H_2S may decompose to S_2 and H_2 in typical Claus-type operations.

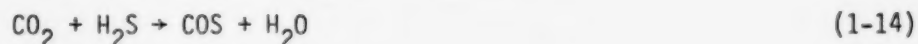
Only the initial rate of reaction of H_2S with a clean limestone surface can be treated in this manner; however, since the layer of CaS which builds on the surface resists the diffusion of H_2S and thus changes the reaction mechanism.

The H_2S formed in the reducing zone can react in the following ways:

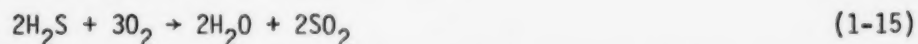
Shift to COS and H_2



Reduce CO_2 to form COS and H_2O :



Oxidize to SO_2 and H_2O :



These reactions occur for the main part by a complex free radical mechanism, which is beyond the scope of this paper. One should note, however, that the actual conversion of H_2S to COS and SO_2 depends to a great extent on the quality of mixing of the H_2S with the air and therefore

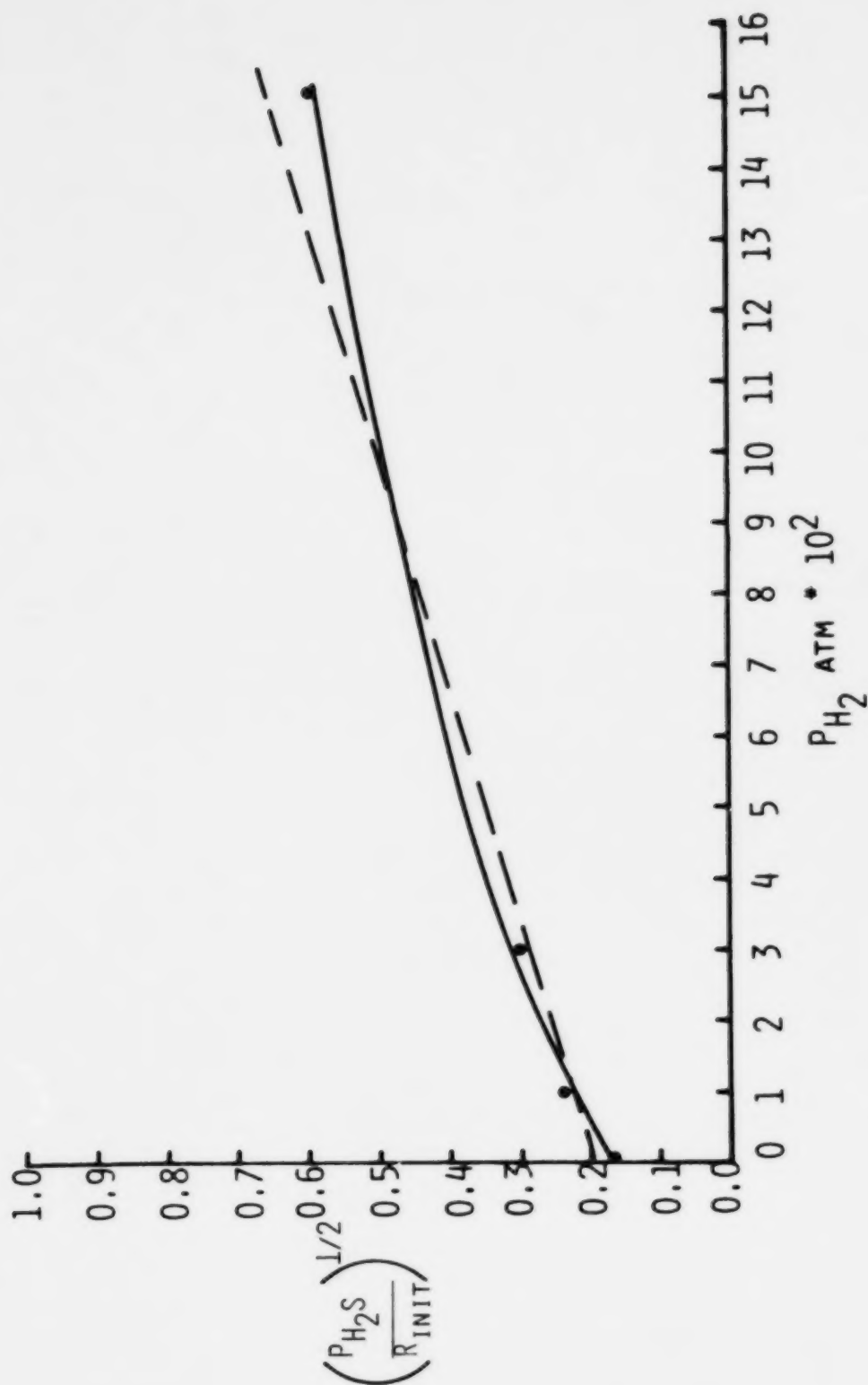
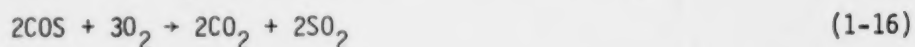


Figure 1.6 $(P_{\text{H}_2\text{S}}/P_{\text{init}})^{1/2}$ vs. P_{H_2} for the system $\text{H}_2\text{S} - \text{CaCO}_3$

on the type of burner used and the fluid mechanics of the system. The COS oxidizes to CO_2 and SO_2 somewhat slower than H_2S .



For calculation purposes, one may assume that the local concentrations of the sulfur-containing gases are determined by the equilibrium composition with the reducing and/or oxidizing species in that vicinity. Kinetics calculations using all the free radical reactions are hopeless since our ability to quantitize the level of turbulence in the combustor is very limited and its effect on the local radicals concentration is immense.

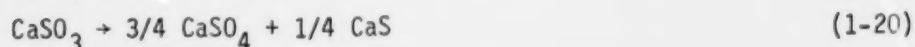
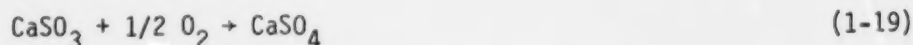
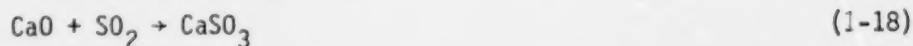
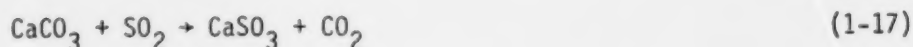
1.6 REACTIONS OF SULFUR-CONTAINING GASES WITH CALCIUM-CONTAINING MINERALS--OXIDIZING ZONE

The following phenomena have to be addressed:

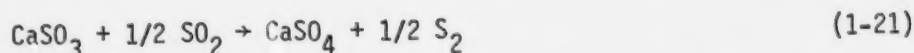
1. The reactions of sulfur dioxide and sulfur trioxide with calcium oxide and carbonate (Table 1.4).
2. The rates of decomposition of calcium sulfate and sulfite (Table 1.4), and how they are influenced by impurities, the mineral components of the coal and temperature.
3. Changes in the solid pore structure which occur as a result of the reactions.
4. The reaction of CO and CO_2 to form COS and the rate of reaction of COS with lime.

1.6.1 Reactions of Sulfur Oxides with Limestone or Calcium Oxide

The numerous reactions which may occur between CaCO_3 and SO_2 and O_2 were described by Van Houte and Delmon (1979). The main reactions are:



and:



The mechanism of the crucial step, the reaction of SO_2 with the oxide or the carbonate to form CaSO_3 is not clear; however, it may involve the ion radical SO_2^- (Ono et al., 1979). The data of Ono taken at 77°K on CaO samples which were prepared at the temperature range 800-1400K show that the concentrations of radicals reach a maximum with calcium oxide prepared at 1173K. This could be due to the fact that the 1173K sample had the largest specific surface area. The SO_2^- radical reacts very fast with molecular oxygen to form SO_4^- even at 77K (Ono et al., 1979). It is, therefore, conceivable that at combustion temperatures the reaction which forms the intermediate MONOVALENT ion SO_4^- is "instantaneous."

Another complication may involve the crystalline structures of the various calcium salts. CaO and CaS are cubic, CaSO_4 is rhombic, and CaSO_3 is hexagonal. The different forms are not miscible and thus every transformation of one compound to another will require a phase transformation, i.e., the nucleation of a new phase. Such processes may restrict the apparent rate of the chemical reaction as demonstrated by Attar and Dupuis (1979).

Calcium sulfite is not stable at coal combustion temperatures and decomposes rather rapidly to CaO and SO_2 . Recently, Cubicciotti et al. (1977) measured the equilibrium vapor pressure of CaSO_3 and used it to calculate its thermodynamic properties. From their data, the equilibrium vapor pressure of CaSO_3 is $8.716 \cdot 10^{-2}$ atm at 1000K, is 4.32 atm at 1500K, and is 30.42 atm at 2000K. Thus, even at 1000K the concentration of SO_2 in atmospheric pressure combustion would have to be at least 87,160 ppm to maintain CaSO_3 intact. Calcium sulfite may be converted to the sulfate by disproportionation (reaction 1-2) or by reacting with oxygen (reaction 1-19). Both reactions are initially chemically controlled and subsequently diffusion controlled, when pure CaSO_3 is reacted (Van Houte and Delmon, 1978 and 1977).

It is not immediately obvious which rate parameters should be used to describe the conversion of the surface CaSO_3 formed during combustion to CaSO_4 . It is logical to assume that reaction (1-19) will be the most important one. The author of this paper recommends the use of equation (1-22), which was derived from his own unpublished data and which describes Van Houte's and Delmon's initial data rather closely.

$$-\frac{d\alpha}{dt} = 8.172 \cdot 10^7 e^{-\frac{39000}{RT}} P_{O_2} S_G \quad (1-22)$$

where P_{O_2} is in atmospheres and S_G is the instantaneous specific surface area of the original CaO (m^2/gm). This equation is consistent with the following assumptions:

- All the surface area is available for reaction with SO_2 .
- The surface reaction between CaO and SO_2 is very fast and is therefore in equilibrium (consistent with Ono et al.'s (1974) data), and
- The rate-limiting step is the reaction of the surface with O_2 .

Note that these assumptions hold only relative to the TRUE chemical kinetic rate, since they do not reflect the buildup of a layer of CaSO_4 on the surface which blocks the diffusion of SO_2 . This process has to be dealt with as described below.

1.6.2 The Rate of Decomposition of Solid Calcium and of Sulfated Calcium Compounds

Part of the sulfur released during coal combustion reacts with naturally occurring calcium compounds and additives. However, since calcium sulfate is not very stable thermally, the final sulfur content of the ash depends also on the rate of decomposition of calcium sulfate and of sulfated ash. Baker and Attar (1981) measured the rate of decomposition of pure and contaminated calcium sulfate and of sulfated ashes. Their main conclusions from the referenced paper and from unpublished data were that:

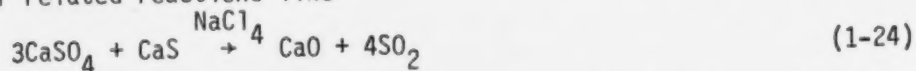
- Pure calcium sulfate decomposes reasonably rapidly at temperatures above about 1323K.
- The rate of the decomposition at temperatures below 1353K is initially kinetically controlled and, as decomposition progresses, becomes diffusion controlled.

- C. The rate of decomposition at temperatures above about 1353K appears to accelerate with conversion. The reason why the initial rate of decomposition is slower than the final rate may be because the CaO formed initially has to nucleate as a new phase, but after some crystallites of CaO nucleate, new CaO can easily build the crystallites up. Also, CaSO_4 is rhombic below 1466K where it transforms into monoclinic. The monoclinic calcium sulfate may decompose at the faster rate than rhombic calcium sulfate.
- D. Lau et al. (1977), who measured the equilibrium vapor pressure of SO_2 over CaSO_4 , suggest that the sulfate ion decomposes to SO_2 and O_2 . They also propose that the vapor pressure of CaSO_4 in the temperature range of 1143-1273K be correlated by the equation:

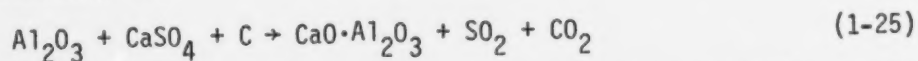
$$\ln P \text{ (atm)} = 8.84 \pm 0.06 - \frac{17287 \pm 74}{T} \quad (1-23)$$

The enthalpy of the decomposition is approximately 510.4 kJ/mole (122.1 kcal/mole).

- E. Baker and Attar (1981) and references therein suggest that CaSO_4 reacts with clays and quartz in the temperature range 1073-1673K. Metal oxides like Fe_2O_3 , potassium salts and many sodium salts significantly increase the rate of decomposition of CaSO_4 and the rate of related reactions like



In the presence of carbon, alumina reacts with calcium sulfate according to:



Baker and Attar (1981) found that carbon and other reducing agents initially accelerate the decomposition of CaSO_4 but they also reduce it to CaS. Therefore, when a sufficiently thick CaS layer is formed on the CaSO_4 , the sulfate decomposition rate becomes diffusion limited and thus the decomposition essentially stops. This may explain the data of Attar (1978a) who found sulfide in coal ash from fuel-rich combustion. Freund et al. (1980) also observed that more sulfur is retained in coal ash and in calcium-containing additives when some unburned carbon is retained in the ash.

Kinetic equations that can adequately describe the rate of decomposition of sulfated ash and of calcium-containing additives are hard to derive and should be examined very carefully. The equations that describe the decomposition of pure CaSO_4 often cannot be used, because pure CaSO_4 is more stable than sulfated ash. In addition, the sulfation of calcium-containing materials occurs on their surface while the bulk volume of the solid CaO adsorbant often remains unsulfated.

Studies on the decomposition rate of CaSO_4 often begin with pure whole crystals of CaSO_4 . The author of this paper uses in his modeling studies the equations below (Attar, 1982). (Valid in the temperature range 973-1673K with an accuracy of $\pm 10\%$).

$$X = 1 - 6.7880 \cdot 10^6 e^{-\frac{3.2179 \cdot 10^4}{t}} \quad (1-26)$$

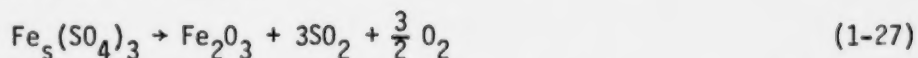
applicable to lignite ash with about 16% CaO and 3.5% Fe_2O_3 and 0.25% K_2O . t is in seconds, X is the fraction of the original ash sulfate sulfur added during the combustion.

The proposed equation reflects the extreme temperature sensitivity of decomposition of surface sulfate. The activation energy for the decomposition of sulfated ash is about 267.3 kJ/mole (63.94 kcal/mole) vs. about 121.5 kJ/mole (29 kcal/mole) for the initial rate of decomposition of pure bulk rhombic CaSO_4 .

The decomposition reaction of calcium sulfate cannot be neglected when the ash or the sulfated calcium additives spend appreciable time in zones where the temperature is larger than, say, 1000°C and/or where the coal or the combustion additive contains significant amounts of potassium or sodium chlorides. This phenomenon should be considered very carefully when laboratory or small burner data are compared with large burner data, since such facilities often differ significantly in the way in which the sulfated solids are cooled and collected.

Iron sulfate is much less stable thermally than calcium sulfate (Attar, 1978) and decomposes around 490-635°C (Mu and Perlmutter, 1981). Therefore, sulfur that is trapped by reacting with the iron to form FeSO_4 may be released again as SO_x when the FeSO_4 or $\text{Fe}_2(\text{SO}_4)_3$ particles

pass through a hot zone.



Since iron oxides tend to physically adsorb sulfur oxides (Baker and Attar, 1981), some sulfur may be retained in the ash as adsorbed sulfur, which may desorb slowly when the ash is dumped in sulfur-oxide-free air.

1.7 THE SOLID PORE STRUCTURE AND THE FORMATION OF NEW SOLID PHASES: QUALITATIVE PICTURE

The difference in the molar volume of the solid products and reactants of the various gas-solid reactions plays a critical role in determining the rate of trapping of sulfur and the total sulfur retained in the ash. Therefore, despite the fact that some aspects of these phenomena were already mentioned, the main points will be reviewed below.

Consider a solid calcium carbonate, CaCO_3 , particle which is thermally decomposed to CaO . If the gross size of the particle remains unchanged, its porosity will be approximately 0.517.

$$\epsilon = 1 - \frac{V_{\text{CaO}}}{V_{\text{CaCO}_3}} = 1 - \frac{M_{\text{CaO}}}{\rho_{\text{CaCO}_3}} \frac{\rho_{\text{CaCO}_3}}{M_{\text{CaCO}_3}} = 1 - \frac{56.08 \cdot 2.93}{3.32 \cdot 100.09} = 0.517 \quad (1-28)$$

Many calcines from natural limestones and calcites indeed have porosities close to the theoretical value, as can be easily calculated from the data of Borgwardt (1970a and 1970b) and Borgwardt and Harvey (1972). The initial porosity of the limestone affects the porosity of the calcine (Borgwardt and Harvey, 1972) but the bulk of the porosity is formed as a result of the calcination. Extended heating of the calcine at high temperatures tends to sinter the pores, however, as mentioned previously (Fischer, 1955).

Since one mole of CaO or CaCO_3 can form only one mole of CaS or CaSO_4 , a complete sulfidation of one mole of CaO or CaCO_3 would change their volumes from about 16.49 and 34.16, respectively, to 28.86 cm^3/mole . Since sulfidation occurs at pulverized fuel conditions after the CaCO_3 is completely decomposed to CaO , the reaction product, CaS , occupies

a larger volume than the reactant, CaO. The magnitude of the expansion is approximately 42.86%. Thus, when a porous CaO particle enters the H₂S-containing gas in the combustion-reducing zone, its surface is slowly converted to CaS and the porosity of the surface gradually decreases due to the volumetric expansion. This reduces the accessibility of the interior pores to the H₂S and thus the apparent rate of sulfidation decreases. This phenomenon is even more significant when sulfation of CaO in SO₂ is considered, since the molar volume of CaSO₄ is about 45.99 cm³/mole and the expansion is 64.15%. Therefore, the porosity of the calcine limits in a sense its capacity to retain sulfur, as was illustrated by Potter (1969), by Borgwardt (1970a, 1970b) and by Borgwardt and Harvey (1972).

Since the molar volume of CaS is smaller than that of CaCO₃, a CaO particle that was formed by the decomposition of CaCO₃ can be converted completely to CaS, provided that the CaO particle retained the original gross volume of the CaCO₃ particle. The temperature has to be, however, larger than about 640°C. Otherwise, the reaction will stop after a 60 Å layer of CaS was formed on the surface. (See Attar and Dupuis, 1979.) In contrast, since $V_{\text{CaSO}_4} = 45.99 \text{ cm}^3/\text{mole}$ and $V_{\text{CaCO}_3} = 34.16 \text{ cm}^3/\text{mole}$, only 0.62 of the CaO can be converted to CaSO₄, provided that the CaO particle does not shrink or expand.

$$X = \frac{1 - \frac{56}{100} \frac{\rho_{\text{CaCO}_3}}{\rho_{\text{CaO}}}}{\frac{1}{\rho_{\text{CaSO}_4}} - \frac{56}{136} \cdot \frac{1}{\rho_{\text{CaO}}}} = 0.62 \quad (1-29)$$

One simple implication of this discussion is that it is desirable to trap as much sulfur as possible on the calcium-containing compounds in the reducing zone, since the molar volume does not impose restrictions on the maximum conversion possible; i.e., even a complete conversion of a CaO particle to CaS will leave material with a theoretical porosity of $\epsilon = 0.155$, provided that no shrinkage occurs.

$$\epsilon = \frac{34.16 - 28.86}{34.16} = 0.155$$

Further implications of these phenomena for coal combustion and

gasification are discussed below. Figure 1.7 shows the relationships between the molar volumes and the closing and opening of pore.

1.8 MODELING OF SULFUR TRAPPING ON CALCIUM-CONTAINING COMBUSTION ADDITIVES

Several models were proposed to explain the apparent rate of reaction of porous calcines with sulfur dioxide. The two most frequently used approaches are: A) the grain model and B) the single pore model. No detailed derivation of the models will be presented and, except for the main assumptions of each model, the discussion will concentrate on the applicability of the model to sulfur oxide trapping.

1.8.1 Grain Model

The "grain model" (Szekely and Evans, 1970; Sohn and Szekely, 1972) was used by Pigford and Sliger (1973) to explain the apparent rate of reaction of SO_2 with CaCO_3 . The model appears to give a reasonable representation of experimental data, provided that certain empirical parameters are properly chosen.

The basic assumptions of the grain model are:

1. The solid consists of an assembly of small uniform grains of reactive adsorbant.
2. The reactive gas can diffuse between the grains and the reaction products form a layer on the grain surfaces which also reduces the rate of reaction.
3. The reaction of the gas on the solid surface is instantaneous.
4. The diffusivity of the gas in the pores is the same as in the bulk.
5. The reactions are isothermal.

The main equations of the model, as presented by Pigford and Sliger (1973), are:

$$\frac{D}{\tau} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) = \frac{\partial \epsilon}{\partial t} + S_v V \quad (1-30)$$

Mass balance around a single grain:

$$4\pi \rho_s (a-x)^2 \frac{dx}{dt} = \frac{D_s}{X} 4\pi a(a-x)c \quad (1-31)$$

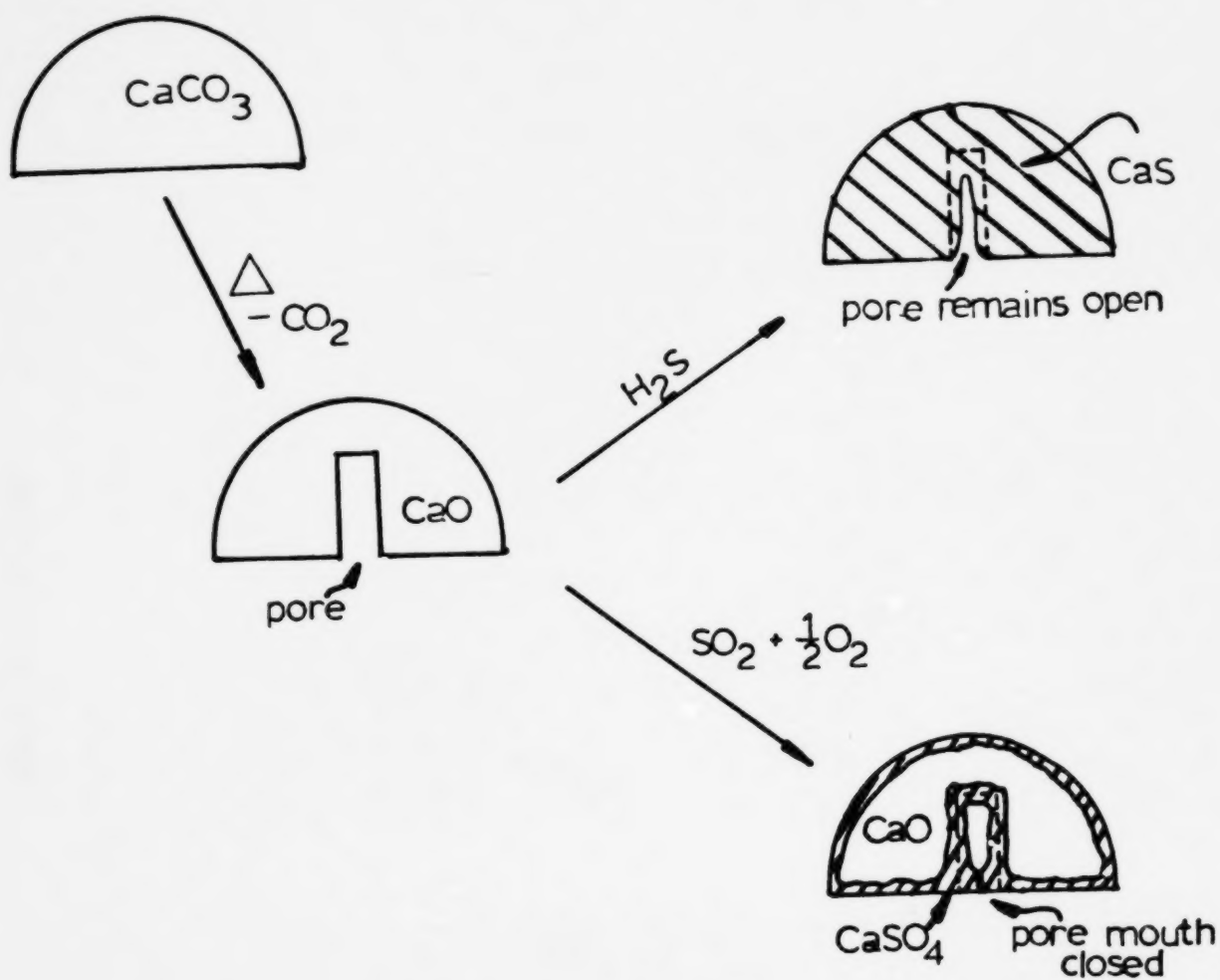


Figure 1.7 Molar-volume pore-volume relationships in the reactions of H_2S and SO_2 with CaO

with the boundary conditions:

$$c(R,t) = C_0 \quad (1-32)$$

$$c(r,0) = 0 \quad (1-33)$$

$$\text{and } \frac{\partial c}{\partial r}(0,t) = 0 \quad (1-34)$$

Despite the moderate agreement between the model predictions and experimental data after adjusting some parameters, the applicability of the model should be carefully evaluated because its results are very sensitive to the values assumed for some of its parameters. These parameters cannot be evaluated independently without using kinetic tests. In the solution obtained by Pigford and Sliger (1973), the porosity, ϵ , and the tortuosity, τ , were assumed constant. This is untrue in the case of the reaction between $\text{SO}_2 + \text{O}_2$ and CaO since the molar volume of the reaction product, CaSO_4 , is larger than that of the reactant CaO , and thus the porosity decreases as the reaction progresses. Moreover, the porosity decreases faster near the particle surface relative to the particle interior. Thus, the porosity and the tortuosity vary as a function of both the particle radius and time.

1.8.2 Pore Model

The single pore model was used by Ramachandran and Smith (1977) and by Chrostowski and Georgakis (1980) to account for the apparent rate of reaction of sulfur dioxide with calcium-containing compounds. The most important assumptions of the model, as listed by Ramachandran and Smith (1977) and by Szekely and Evans (1970), are:

1. The pore is cylindrical, of finite length and a uniform original radius, r .
2. Each pore has a cylindrical solid associated with it with overall radius λ .
3. The concentration of gas A does not vary radially in the pore.
4. The concentration of gas A within the solid-product layer is assumed to vary only in the radial direction and there is no axial diffusion of A in the product layer.

5. The chemical reaction is irreversible and first order with respect to gas A and first order with respect to the interfacial surface of B.
6. Isothermal conditions prevail.
7. External mass-transfer resistances are neglected.
8. The solid reactant is nonporous and the reaction occurs on a sharp interface.

The key equations which were used by Ramachandran and Smith to describe the conversion of the solid include material balance on the gas in the pore:

$$D \frac{d}{dx} (r-1)^2 \frac{dc}{dx} = 2c \frac{1}{k(r+\delta)} + \frac{\ln \frac{r+2}{r-1}}{D_e} \quad (1-35)$$

and material balance on the solid:

$$(r-1)^2 = (1-\gamma)(r-\delta_2)^2 + \gamma r^2 \quad (1-36)$$

or in a differential form:

$$(r-1) \frac{d\delta_1}{dt} = (\gamma-1)(r+\delta_2) \frac{d\delta_2}{dt} \quad (1-37)$$

with the boundary conditions:

$$c = c_0 \text{ at } X = 0 \quad (1-38)$$

$$\frac{dc}{dx} = 0 \text{ at } X = L \quad (1-39)$$

$$\delta_1 = \delta_2 = 0 \text{ at } t = 0 \quad (1-40)$$

The local conversion n is given by:

$$n(x) = 1 - \frac{\lambda^2 - (\delta+\delta_2)^2}{\lambda^2 - r^2} \quad (1-41)$$

and the average conversion for the pore, $\bar{n}$, is:

$$\bar{n} = \frac{1}{L} \int_0^L 1 - \frac{\lambda^2 - (r+\delta_2)^2}{\lambda^2 - r^2} dx \quad (1-42)$$

The numerical solution of the model appears to represent the data of Hartman and Coughlin (1974), which were taken around 800°C, reasonably well for conversions smaller than about 30% CaO.

1.8.3 Modeling of Sulfur Trapping in Fluidized Bed Combustion

Several attempts were made to model sulfur retention based only on the properties of the calcium-containing additives (e.g., Bethell et al., 1973; Horio and Wen, 1976); however, the actual combustion process has to be taken into consideration in such models. Chen and Saxena (1977), Rajan et al. (1978) and others developed models that describe sulfur trapping in a fluidized bed combustor.

The model of Chen and Saxena (1977), as well as the model of Rajan et al. (1978), appear to describe the limited available data reasonably well. However, both models use adjustable parameters which restrict their usefulness.

1.9 IMPLICATIONS OF THE DYNAMICS OF LIMESTONE AND AIR INJECTION FOR SULFUR TRAPPING

The calculations shown previously suggest that a complete decomposition of limestone particles occurs in a time scale of the order of 10^{-3} -1.0 s for typical PFC temperatures and limestone particles of 5-200 microns. Since during the decomposition of CaCO_3 gaseous CO_2 evolves, it may be assumed that neither H_2S nor SO_2 molecules can approach the surface, and no sulfurization of the solid occurs until the decomposition of the carbonate is complete. Therefore, if the limestone particle completes decomposing in the reducing zone, it will react with H_2S and may be completely converted to CaS . However, if the limestone particle does not completely decompose in the reducing zone, it will be carried to the oxidizing zone where it will continue to decompose to CaO and subsequently react with SO_2 to form CaSO_4 . Since volume changes restrict the conversion of CaO to CaSO_4 , it is desirable to have the limestone particles decompose completely to CaO and react to form CaS in the reducing zone, rather than be sulfated to CaSO_4 in the oxidizing zone.

The length of the reducing zone is determined by the rate of pyrolysis of the coal particles injected into the combustor, the rate of heat transfer achieved, and the level of mixing of air and combustibles.

Moreover, the proximity of the limestone or CaO particle to the carbon also influences the mechanism of reaction, i.e., whether the sulfurization occurs in the reducing or in the oxidizing zone.

In real combustion, the effective length of the reducing or oxidizing zones depends, of course, on the rate of heating and on the flow rates of gas around the coal particles. Moreover, trapping of sulfur by the reaction of CaO with H_2S can occur only if the $CaCO_3$ particle finished decomposing to CaO while the coal particle is still releasing H_2S .

In other words, CaS can form only when the H_2S and CaO exist in the combustor close in time and space. Thus, a maximum amount of CaS can be formed if the rate of heating of the coal and the limestone particles can be adjusted so that a maximum contact time is available for the H_2S and the CaO at the temperature range 800-1100°C.

Our finding suggests that the largest level of trapping of sulfur can be achieved when the calcium is distributed in the coal particle in a finely divided form. Also, for reasons previously explained, the retention of sulfur is larger when unburned carbon residue is left with the ash. Complete mixing of the air with the coal-limestone injected into the furnace decreases the trapping of sulfur by reducing the length of the reducing zone.

1.10 TRAPPING OF SULFUR IN COAL ASH

Analysis of coal ashes from power plants and from laboratory ashing tests suggests that some sulfur is retained in the ash, primarily as sulfate, although some physically adsorbed sulfur gases are also found. (Baker and Attar, 1981). Conclusions regarding sulfur trapping in ash include:

1. More sulfur is trapped when the ash contains more calcium.
2. Ion-exchanged calcium is more effective than calcite or dolomite in trapping sulfur.
3. More sulfur is found in ash with more sodium and potassium; however, more sodium and potassium in the coal does not guarantee that more will be in the ashes.

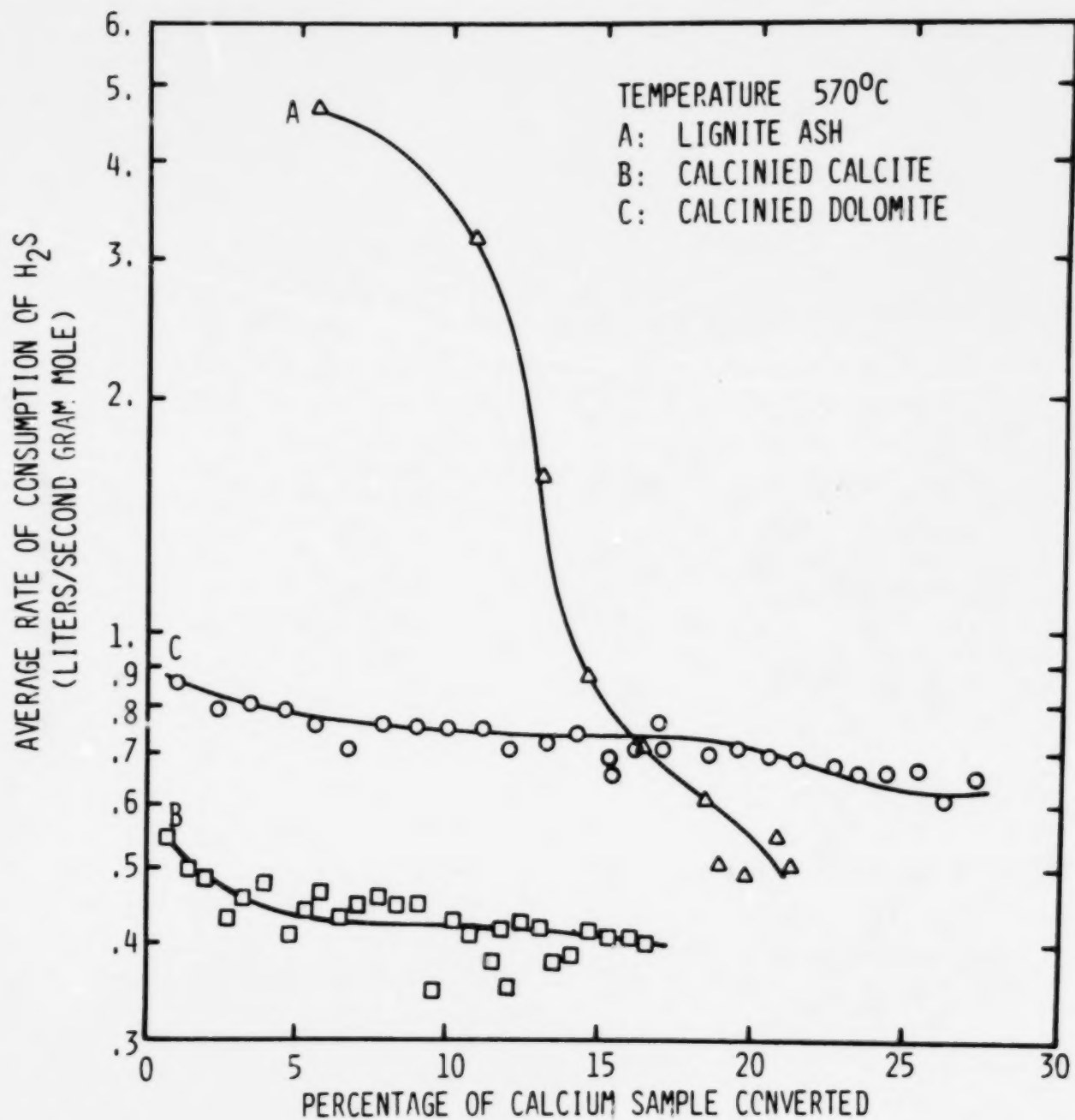


Figure 1.8 Rate of reaction of H_2S with calcined calcite, dolomite and lignite ash at 570°C

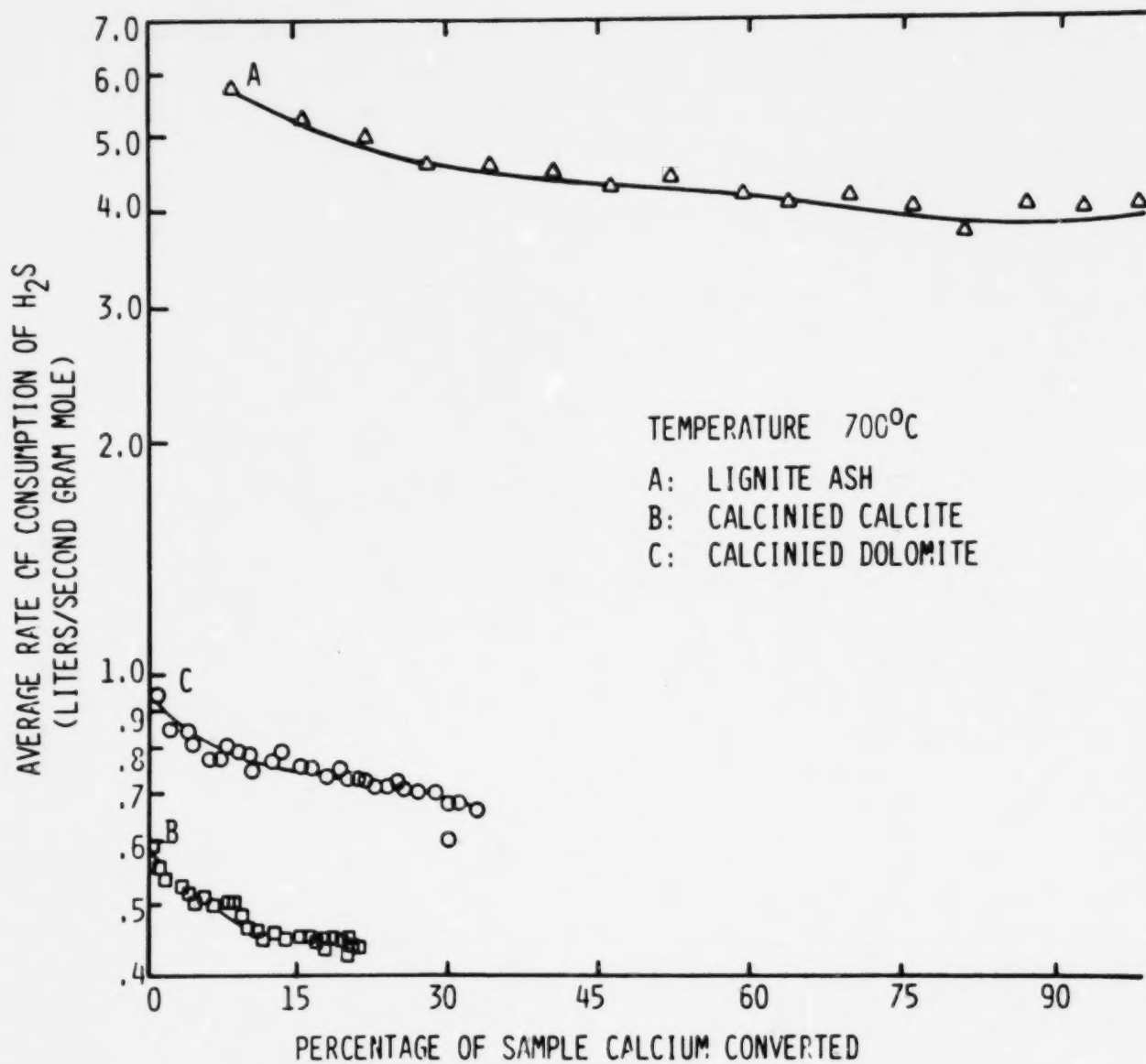


Figure 1.9 Rate of reaction of H_2S with calcined calcite, dolomite and lignite ash at 700°C

4. More sulfur is retained in the ash when the combustion is incomplete and some carbon is retained with the ash.

Since ash can react with sulfur-containing gases, different investigators examined the possible use of coal ash to sweeten or desulfurize gas. In the first case, the gas contains H_2S and reacts with the ash to form predominantly CaS and FeS . In the second case, the ash reacts with sulfur dioxide and oxygen to form calcium sulfate. When the reaction temperature is below $490^{\circ}C$, iron sulfate may also be formed. When the reaction temperature is below $300^{\circ}C$, some sulfur dioxide may physically adsorb onto the iron oxide surface. Since only a small fraction of the ash, the basic components, can react with the acidic sulfur-containing gases, in most cases, only a fraction of the coal sulfur can be retained in the ash even if all the basic elements could have reacted. Bituminous coals in general do not have sufficient calcium in their ash to allow complete trapping of sulfur. However, many lignites, e.g., Texas lignite from the Wilcox formation, have sufficient calcium to trap all the sulfur (Attar, 1978).

Figures 1.8 and 1.9 show the rate of reaction of lignite ash and of calcined dolomite and calcite with hydrogen sulfide at $843K$ ($570^{\circ}C$) and at $973K$ ($700^{\circ}C$) (Attar, 1978). In both cases the ash reacts 5-10 times faster than the pure calcined carbonates. The rate of reaction at $843K$ drops sharply after only about 15% of the ash calcium has been converted; while at $973K$ it was possible to convert all the ash calcium sulfide at a rate 5-10 times faster than that of the conversion of the pure calcines (Attar, 1978).

The rate of reaction of sulfur dioxide with ash at temperatures larger than $673K$ is fast, however, complete conversion of the ash calcium to calcium sulfate is impossible. Moreover, some of the sulfur is retained on the ash in the form of adsorbed sulfur dioxide. It is believed that the adsorbed sulfur is retained on the iron oxide (Baker and Attar, 1981). The adsorbed sulfur dioxide desorbs slowly even at room temperature, so that care should be taken in disposing of high-sulfur high iron ash (Baker and Attar, 1981).

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1.13 NOMENCLATURE

A	- particle surface area
a	- grain radius
C	- gas concentration
C_o	- surface concentration of gas
C_{p1}	- heat capacity of limestone
C_{p2}	- heat capacity of lime
D	- diffusion
D_e	- effective diffusion coefficient
E	- activation energy
h	- heat transfer coefficient
k	- reaction rate constant
K_1	- equilibrium constant of elementary rxn step
K_2	- equilibrium constant of elementary rxn step
K_3	- equilibrium constant of elementary rxn step
k_b	- backward reaction rate constant
k_f	- forward reaction rate constant
k_g	- mass transfer coefficient in the gas
k_o	- preexponential factor
L	- pore length
M_{CaCO_3}	- molecular weight of $CaCO_3$
M_{CaO}	- molecular weight of CaO
P	- vapor pressure
P_{H_2}	- partial pressure of hydrogen
P_{H_2S}	- partial pressure of hydrogen sulfide
P_{O_2}	- partial pressure of oxygen

P_{S_2}	- partial pressure of elementary sulfur
r	- particle radius; except in pore model (eqns. 28-35-pore radius)
$r_{initial}$	- initial rate of reaction
S_g	- specific surface area
S_v	- volumetric rate of reaction
T	- absolute temperature
T_1	- combustion chamber temperature
t	- time
V	- particle velocity
V_{CaO}	- molar volume of CaO
V_{CaS}	- molar volume of CaS

1.14 GREEK LETTERS

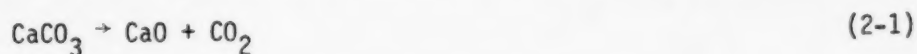
α	- fraction decomposed
γ	- $\rho_{CaO}^P M_{CaS} / \rho_{CaS} M_{CaO}$
δ	- thickness of the product layer
δ_1	- thickness of that part of the product layer measured from the initial position of the pore walls to the pore walls at any time (cm)
δ_2	- thickness of that part of the product layer between the initial position of the pore wall and the reaction interface (cm)
ϵ	- porosity
ϵ_0	- emissivity
λ	- thickness of solid volume associated with a pore of radius r
μ	- local conversion
$\bar{\mu}$	- average conversion

ρ	- molar density of a particle
ρ_{CaCO_3}	- density of CaCO_3
ρ_{CaO}	- density of CaO
ρ_g	- density of gas
ρ_s	- density of solid
σ	- Stefan-Boltzman constant
τ	- tortuosity

CHAPTER 2

IN SITU ANALYSIS OF THE PORE STRUCTURE OF SOLIDS

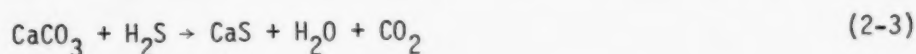
Several processes occur in the LIMB combustor which change the pore structure of the solid. The main reactions which involve the limestone are the decomposition of the limestone to porous lime and CO_2 :



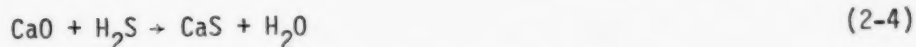
The sintering of the lime to nonporous material:



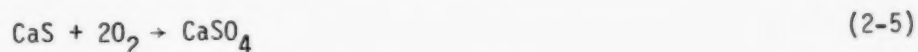
The sulfidation of limestone and of lime in the reducing zone:



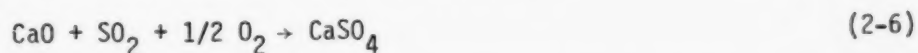
and



Oxidation of the calcium sulfide, CaS , to the sulfate:



and direct sulfation of lime with SO_2 and O_2 :



In all of these reactions the pore volume of the solid changes. In reaction 2-1, pores are formed and enlarged. However, pores near the lime surface are essentially closed by the formation of CaSO_4 in reaction 2-6. Closure of surface pores limits the conversion of the lime to CaSO_4 and thus restricts the trapping of sulfur achieved. Therefore, it is desired to know the pore structure of the solid during the reaction or in conditions as close to the reaction conditions as possible.

Since all of the established methods for pore structure analysis involve low-temperature analysis of the solid using mercury or nitrogen penetration techniques, it is impossible to use them to determine the status of the porous lime at the reaction conditions. Thus, a program was initiated to address some of the questions associated with the transformations of the limestone pore structure of the limestone.

2.1 OBJECTIVES AND STRATEGY

The objectives of this task were:

- 1) to devise a method to determine the pore structure of solids which can be used at high temperatures.
- 2) to determine the range of variables in which the method can be used and to compare its results with established methods for pore-structure analysis, and
- 3) to apply the method to determine structural changes in lime and limestone during their reaction with H_2S and SO_2 .

General Appendix A describes verification tests that were conducted on HDS catalysts with a known pore structure that were supplied to us by the U.S. DOE.

2.2 THE PULSE DISPERSION METHOD (PDM) FOR IN-SITU PORE STRUCTURE ANALYSIS

2.2.1 Qualitative Description

The essence of the PDM method is as follows: a column (reactor) is packed with the solid and is heated to the desired temperature in a stream of the desired gas. Whenever a measure of the pore structure is needed, a pulse of inert or reactive gas is injected to the reactor inlet and its dispersion is measured at the reactor outlet. The dispersion of the pulse is determined by a variety of factors as will be described below, including the pore structure of the solid. Therefore, the shape of the dispersed pulse includes information on the pore structure of the solid, which can be retrieved if a proper analytical technique is used. Figure 2.1 is a schematic diagram of the experimental system.

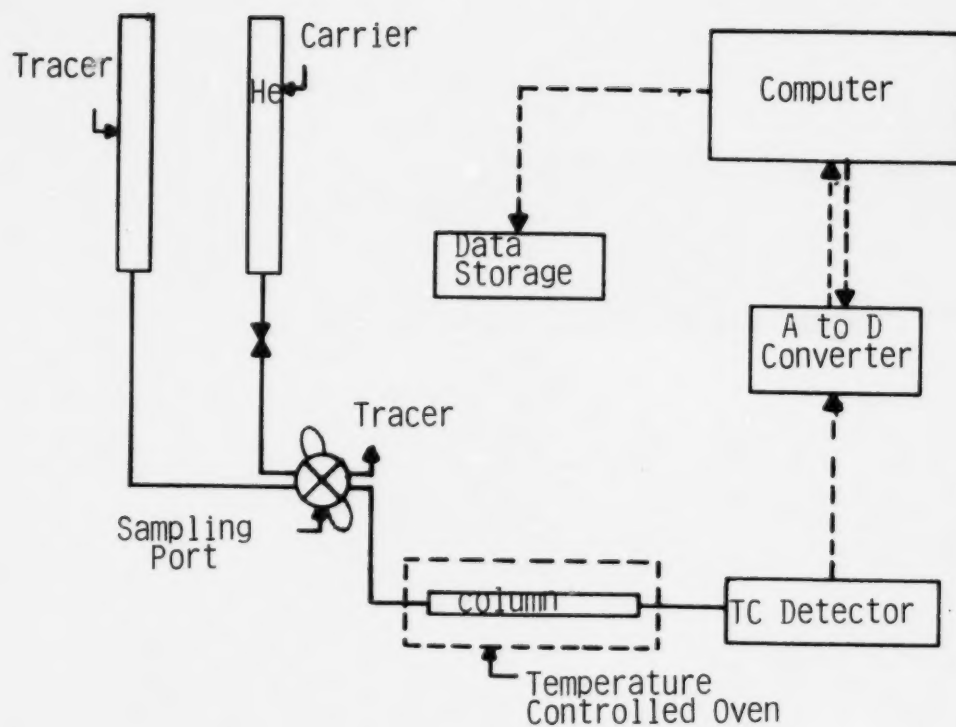


Figure 2.1
Schematic Diagram of Experimental Apparatus
Used for Measuring Pulse Dispersion

The analytical method which was adopted assumes that the pulse flows in the reactor and behaves like an ideal gas. The adsorption isotherm is assumed to be linear and the dead volume dispersion small. Under these circumstances, the Kubin-Kucera model (KKM) can be applied to the flow. Thus, the KKM model is solved for the pulse in the Fourier (frequency) domain which permits obtaining the Fourier coefficients of the outlet dispersed pulse as a function of the column and solid parameters. A search technique is applied which finds the best column flow and solid properties values which describe the pulse in the complex variable domain. The values of the parameters should be independent of the fact whether their evaluation was done in the time or the frequency domain. However, in order to ensure that we converge on the correct values of the porosity, diffusivity, etc., we revert back to the time domain and compare the experimental pulse with the one obtained by the search. In general, the agreement and the reproducibility are excellent.

The PDM method is a dynamic technique and thus an extensive verification was needed to assure that the results obtained were independent of the method and that they correlated with established techniques for pore structure measurements.

2.2.2 Mathematical Model

The objective of the mathematical model is to quantify the dependence of the pulse residence time distribution on pore structure related interactions. The model which is considered here was originally set forth by Kubin and Kucera (2.1). A slightly modified version which is discussed by Schneider and Smith (2.2) is shown here.

Theory

The concentration, $c(z,t)$ of the adsorbing gas as a function of time and axial position in the bed can be obtained by solving the following system of equations: mass balance of the adsorbable component in the gas phase:

$$\frac{E_A}{\alpha} \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z} - \frac{\partial c}{\partial t} - \frac{3D}{R} \frac{1 - \alpha}{\alpha} \left(\frac{\partial c_i}{\partial r} \right)_{r=R} = 0 \quad (2-7)$$

mass balance of this component in the particle

$$\frac{D_c}{\beta} \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{2}{r} \frac{\partial c_i}{\partial r} - \frac{\partial c_i}{\partial t} \right) - \frac{\rho_p}{\beta} \frac{\partial c_{ads}}{\partial t} = 0 \quad (2-8)$$

rate of adsorption (assumed to be linear)

$$\frac{\partial c_{ads}}{\partial t} = k_{ads} (c_i - c_{ads}/K_A) \quad (2-9)$$

external diffusion boundary condition

$$D_c \left(\frac{\partial c_i}{\partial r} \right)_{r=R} = k_f (c - c_i) \quad (2-10)$$

internal diffusion boundary condition

$$\frac{\partial c_i}{\partial r} = 0 \quad \text{at } r = 0 \text{ for } t > 0 \quad (2-11)$$

and the initial conditions

$$c = 0, \quad \text{at } z = 0 \text{ for } t = 0 \quad (2-12)$$

$$c_i = 0, \quad \text{at } r \geq 0 \text{ for } t = 0 \quad (2-13)$$

Conditions (2-12) and (2-13) state that the adsorbent does not contain any adsorbed species at the start of the run. Then condition (2-14) specifies that at the bed inlet the concentration of the adsorbable species is maintained constant. For a brief but finite time, t_{oA} , which approximates the inlet pulse function

$$c = c_0 \quad \text{at } z = 0 \text{ for } 0 < t < t_{oA} \quad (2-14)$$

$$c = 0 \quad \text{at } z = 0 \text{ for } t > t_{oA}$$

Two very critical assumptions are implicit in this model. These are: 1) the effective intraparticle diffusivity is concentration

independent; 2) the adsorption process is linear, i.e., follows a Henry's law dependence. These critical assumptions must be verified during the course of all experimental work. These two assumptions become increasingly valid as the concentration of the injected pulse diminishes. The concentration of the tracer component in the pulse may be varied by diluting it with carrier gas. This may be accomplished by pre-mixing the components in a cylinder or piston, or by metering the flows of the tracer and carrier gas through the injector port. For each tracer gas used, it is suggested that a series of dilutions should be pulsed through the column to determine the appropriate operating range with respect to pulse concentration. The appropriate operating range will be such that a change in concentration of tracer has no appreciable effect on residence time distribution (see Figure 2.2).

2.2.3 Method of Characterizing the Pulse Shape

The shape of the pulse contains information relevant to the interaction of the pulse with the solid. In order to quantify this information, a method must be chosen for characterizing the pulse shape or residence time distribution. This method must also be expressible in terms of mathematical formulations of the model. Two accepted methods for characterizing pulse shape, i.e., residence time distributions, are the moment method and the Fourier coefficient method.

In each of these methods, the analysis requires the comparison between experimentally measured pulse characterizing factors (i.e., moments or Fourier coefficients) and those of the model predictions. The flexible parameters of the model are chosen to fit the experimental results.

2.2.3.1 Moment Method

The mathematical operation for measuring moments of the experimental pulse and the model predictions are shown below:

The n^{th} absolute moment, μ'_n , of the function, $c(z,t)$, is defined as

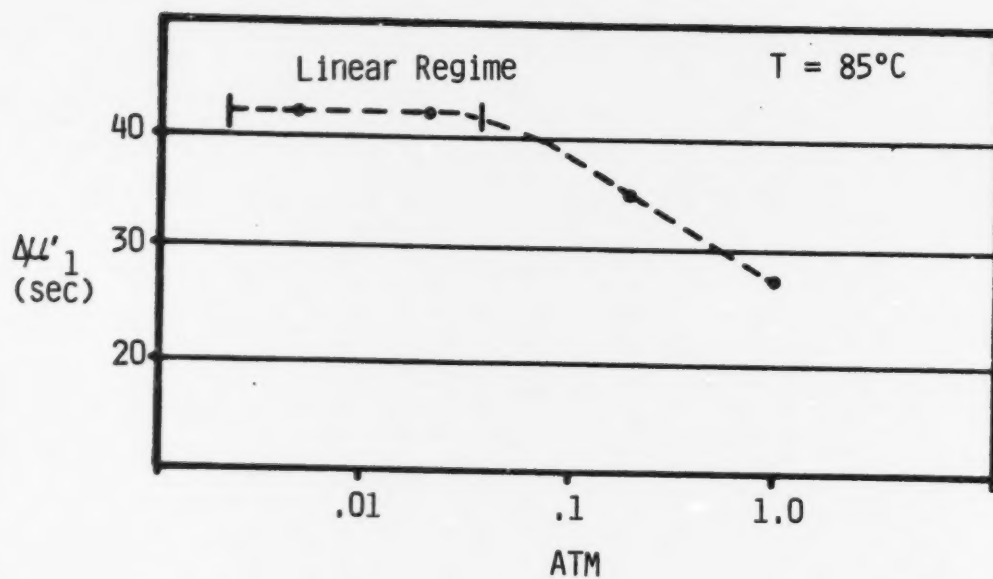


Figure 2.2
Test for Linear Adsorption

$$\mu'_n = m_n/m_0 \quad (2-15)$$

where

$$m_n = \int_0^\infty t^n c(z,t) dt \quad (n=0,1,2,3,\dots) \quad (2-16)$$

The n^{th} central moment μ_n is defined as

$$\mu_n = (1/m_0) \int_0^\infty (t-\mu'_1)^n c(z,t) dt \quad (2-17)$$

(The first absolute moment, μ'_1 , characterizes the position of the center of gravity of the chromatographic curve, whereas the second central moment μ_2 depends on the width of this curve.) The evaluation of the moments from a knowledge of $c(z,p)$ is based on

$$m_n = (-1)^n \lim_{p \rightarrow 0} \frac{d^n}{dp^n} c(z,p) \quad (2-17)$$

By using Equations (2-15) to (2-17), the first absolute, and second and third central, moments (μ'_1, μ_2, μ_3) can be expressed as follows:

$$\mu'_1 = (x/v)(1+\delta_0) + (t_{0A}/2) \quad (2-18)$$

$$\mu_2 = (2x/v) \delta_1 + (E_A/\alpha)(1+\delta_0)^2(1/v_2) + (t_{0A}^2/12) \quad (2-19)$$

$$\begin{aligned} \mu_3 = & (3x/v) \delta_2 + 4(E_A/\alpha)\delta_1(1+\delta_0)(1/v^2) \\ & + 4(E_A/\alpha)^2(1+\delta_0)^3(1/v^4) \end{aligned} \quad (2-20)$$

where

$$\delta_0 = (1-\alpha)\beta/\alpha \quad 1' + (\rho_p/\beta)K_A \quad (2-21)$$

$$\begin{aligned} \delta_1 = & (1-\alpha)\beta/\alpha \left[\frac{\rho_p K_A^2}{\beta k_{ads}} \right. \\ & \left. + \frac{R^2 \beta_f}{15} \left(1 + \frac{\rho_p}{\beta} K_A \right)^2 \left(\frac{1}{D_c} + \frac{5}{k_f R} \right) \right] \end{aligned} \quad (2-22)$$

$$\delta_2 = \lim_{p \rightarrow 0} \frac{d^2}{dp^2} h(p) \quad (2-23)$$

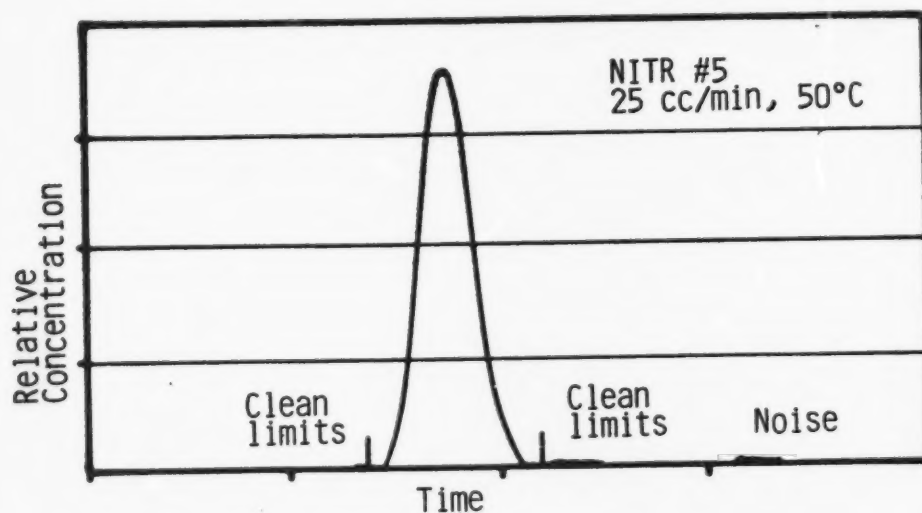
Experimental chromatographic curves of the effluent from the bed can be used in Equations (2-15) to (2-17) to evaluate the moments μ'_1 and μ'_2 . Data at different velocities and particle radii, R , will give the moments as a function of these two variables. Then Equations (2-18), (2-19), (2-21), and (2-22) can be used to evaluate the axial dispersion coefficient, E_A , intraparticle diffusion coefficient, D_c , adsorption rate constant, k_{ads} , mass transfer coefficient, k_f , as well as the adsorption equilibrium constant k_a . In this way all the constants necessary for the analysis are determined.

2.2.3.2 Discussion of the Moment Method

The moment method is limited by the accuracy of measuring higher moments. It is commonly accepted that for most work the third and higher central moments are too error prone for practical application. Conventionally, only the first absolute and second central moments are used. If the pulse response results in a long attenuated tail, then even the second central moment may be of dubious value. Since all detectors have some inherent noise superimposed over the true signal, some criterion must be developed for dealing with it. One criterion which is used is to set the pulse signal to zero if the signal falls below some prescribed small value. This operation avoids the inclusion of a noise background during the computation of moments. For an extended tail, the moment method is highly sensitive to this prescribed lower bound. Consequently, the accuracy of the moment method is strongly tied to the signal to noise ratio of the detector. This is less true of the Fourier method (see Figure 2.3).

In general, then, for a single pulse, the moment method will generate at best two expressions for the evaluation of model parameters. Often more than two parameters in the model are unknown; therefore, moments must be measured for pulses at differing carrier gas velocities. This will then generate enough information to uniquely define the best fit parameters.

<u>NOISE</u>		<u>CLEAN</u>	
MEAN T(SEC)= POWER	26.1224 PHASE	MEAN T(SEC)= POWER	26.0999 PHASE
.999892	1.5708	.999956	1.5708
.993292	-.0317383	.9941	-.0206243
.97442	1.50939	.976378	1.51011
.945499	-.0911391	.942062	-.0906231
.907233	1.45152	.909453	1.45192
.859664	-.147584	.861557	-.146752
.804547	1.39909	.507252	1.39395
.74338	-.174632	.74637	-.196065
.680262	1.3563	.652278	1.35441
.614598	-.233985	.613453	-.234959
.54617	1.32109	.548575	1.32225
.481725	-.257722	.482493	-.239057
.41866	1.30734	.419303	1.30747
.359327	-.263094	.35962	-.262633
.304299	1.3139	.304749	1.31629
.23406	-.242737	.255124	-.237005



Variance (sec²) = 3.6117 Noise
 Variance (sec²) = 3.1412 Clean

Figure 2.3

Comparison of the Effect of Noise on the Moment
 Method and the Fourier Domain Method

POWER	PHASE	POWER	PHASE	POWER	PHASE
1	1.5708	1	1	1	1
.997362	-.159028	.988049	-.336974	.996101	-.236968
.991734	1.25379	.989557	.899631	.989557	.899638
.98112	-.473572	.924737	-1.00779	.977351	-1.00891
.96309	.939061	.968287	.228602	.957707	.220853
.947475	-.790054	.953741	1.4604	.935751	1.46236
.924623	.624492	.935294	-.443066	.91051	-.442203
.829603	-1.10537	.912068	.790346	.876483	.793832
.870301	.308278	.886584	-1.11338	.841057	-1.11223
.837165	-1.41827	.859322	.12097	.802719	.124703
.803423	-7.874838-03	.827516	1.35513	.764857	1.35771

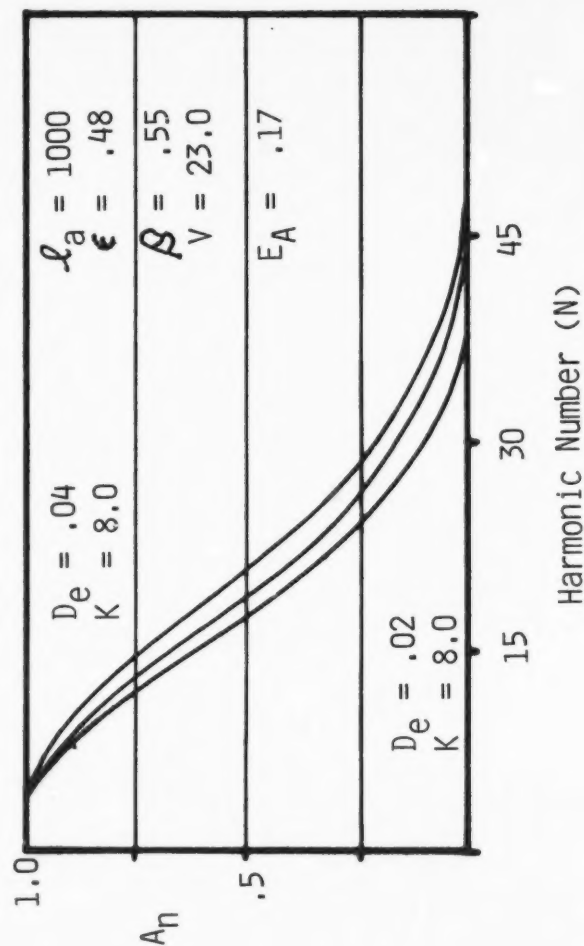


Figure 2.4
Effect of Parameters on Amplitude Ratio and
Phase Lag (Sensitivity)

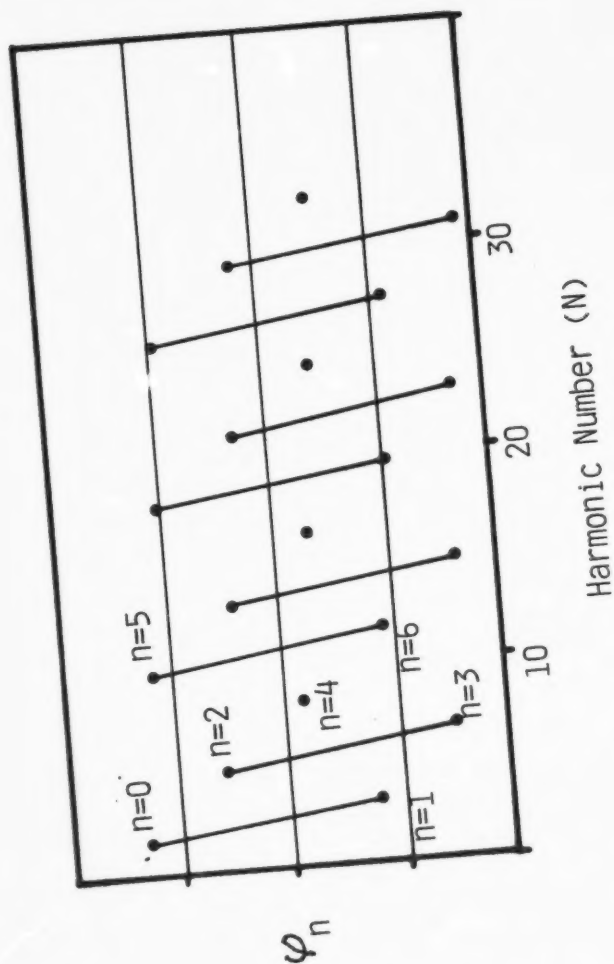


Figure 2.5
Phase Lag of Simulated Pulse
versus Harmonic Number

Since this method involves considerable effort, downtime for detector stabilization, etc., it is less attractive than the soon-to-be-discussed Fourier method. The moment method is often used in this project to provide information in conjunction with that from the Fourier method, to get a feel for the approximate range of the parameters, and to help in providing a close starting point for the parameter search routine used in the Fourier method.

2.2.3.3 Fourier Coefficient Method

The Fourier coefficients of the experimental pulse are measured as follows:

Elements of Theory of Fourier transforms:

Any integrable function $f(t)$ in an interval in t of T can be represented by a Fourier series, e.g.,

$$f(t) = \sum_{n=1}^{\infty} a_n \sin \frac{n\pi t}{T} + \sum_{n=0}^{\infty} b_n \cos \frac{n\pi t}{T} \quad (2-24)$$

where the coefficients of the sine and cosine terms are

$$a_n = \frac{1}{T} \int_0^{2T} f(t) \sin n\pi t/T dt \quad (2-25)$$

$$b_n = \frac{1}{T} \int_0^{2T} f(t) \cos n\pi t/T dt \quad (2-26a)$$

$$b_0 = \frac{1}{2T} \int_0^{2T} f(t) dt \quad (2-26b)$$

The model may be solved for the Fourier coefficients (Appendix A) which depend on the chosen values of the model parameter. Higher frequency coefficients are less affected by noise than are the higher moments. Thus, from a single pulse numerous Fourier coefficients may be evaluated providing sufficient information to fit model parameters in a multi-dimensional search routine.

Rather than fitting Fourier coefficients directly, functions of these coefficients are used. These functions are shown here.

It is convenient to employ the amplitude ratio, A_n , and the phase lag, φ_n , for the n^{th} harmonic component in place of a_n and b_n :

$$A_n = T \sqrt{a_n^2 + b_n^2} \quad (2-27)$$

$$\varphi_n = \arctan (b_n / a_n) \quad (2-28)$$

The technique, then, is to evaluate a_n , b_n and subsequently A_n and φ_n from the normalized chromatograph curve using Equations (2-25) and (2-26).

A number of search techniques have been evaluated by previous investigators such as the conjugate gradient method of Fletcher and Reeves, the Newton-Raphson search, and the Modified Simplex technique of Nelder and Mead. This project has utilized a pattern search routine for preliminary efforts (Appendix B). An example of a fit is shown in Figure 2.6.

2.2.3.3-A. Experimental Technique

A column is first packed with a solid which has been meshed to a narrow size fraction. The solid particle diameter to column diameter should preferably be in the range of 1/10. However, for sensitive measurement of the effective intraparticle diffusivity coefficient, R^2/D_e should be no less than about .1. This may limit the practical size range of the particle. The bed voidage must be measured or calculated by some means (i.e., knowledge of the apparent density of the solid and the packed column weight). The column should be connected to the injector port and detector with a minimum of dead space. If connecting tubing is used, it should be of 1/16" or less and its length minimized. The pressure drop through the column should be minimized, preferably to less than 5% of the absolute pressure of the carrier. Helium is used as a carrier in this project. If measurements are made at elevated temperatures, it is preferable to preheat the carrier gas to the desired temperature before the injector port to insure constant velocity of the carrier in the column.

POWER EXP	POWER MODEL	PHASE EXP	PHASE MODEL
.9999	.999969	1.5708	1.5708
.9964	.996497	.3105	.310437
.9839	.936103	-.95	-.949805
.9689	.968923	.931	.93178
.9456	.945467	-.3284	-.327878
.9106	.916225	1.554	1.55453
.882	.881514	.2955	.295915
.843	.842431	-.962	-.961994
.8	.799536	.923	.922507
.753	.75347	-.333	-.333669
.7038	.705222	1.354	1.55279

Objective Function = Order of 1.05-5 to 1.05-6

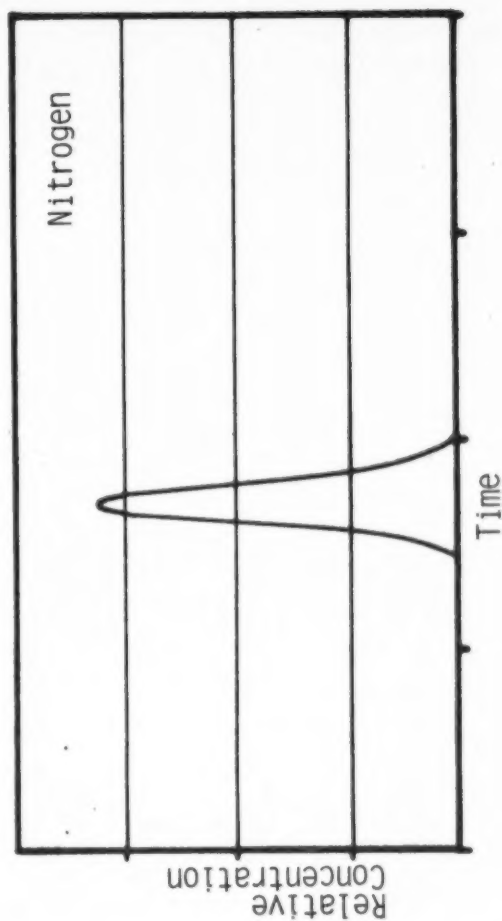


Figure 2.6
Comparison of the Experimental and Model Amplitude
Ratio and Phase Lag

2.2.3.3-B. Pulse Injection and Measurement

When the injector port is actuated (computer control or manually), the analogue to digital converting device is simultaneously actuated. This process may be under complete control of a master laboratory computer code or involve different levels of operator control. In this project, the sample valve was actuated while simultaneously running the pulse collection program 'pulse'. This program initiates the A/D conversion process immediately. It controls the sampling frequency, the time period of sampling, and it calculates Fourier coefficients, moments, etc., once all the data have been stored in an array and the A/D process terminated.

It is suggested that the following criterion for pulse sampling and Fourier coefficient sampling be followed:

- 1) The frequency of pulse sampling should be such that at least 50-100 points characterize the pulse.
- 2) The period of integration used in Fourier coefficient calculation should be 3-5 times the time at which the pulse tail vanishes.

2.2.3.3-C. Test for Sensitivity of Pulse Shape on Parameters

The period of integration, T , used in calculating the Fourier coefficients, and the harmonic number (n) has some bearing on the ability to extract true values for the parameters during the search routine. It is known that for small values of the angular velocity ($w = n/T$), the Fourier coefficients are not very sensitive to the parameters, i.e., many sets of parameters give nearly equal fits and the search routine will run into problems of local minima. On the other hand, for large w the random error contribution increases and the fit may be erroneous. A diagnostic test for using the right range of harmonics is to plot the log of $1/A_n$ versus w^2 . The straight line region at low w is the insensitive region, the scattered region at high w is the error prone region (if present), and the intermediate region should give the best results for fitting purposes.

2.2.3.3-D. Computer Code Description

PULSE

This program controls the logic for sampling the detector signal. A single statement declares the frequency of sampling, the period of sampling, the array name for storing the sampled data in the work space, and which channel to sample from through built-in software contained in the Minc lab computer system. The program also permanently stores the raw data as well as some calculated data on a diskette by opening the appropriate output files. These files may be recalled for further use. The program finds the time of the peak height and calculates the following quantities: 1) zeroth moment, 2) first absolute moment, 3) second central moment, 4) Fourier coefficients, 5) phase lag, 6) amplitude ratio. A time lag may be introduced into the sampling routine so that sample points are only taken near the pulse elution time. The time lag must be accounted for in the integration step. All integrations use a Simpson's rule technique. The raw data (actual pulse signal) and the phase lag and amplitude ratio are visually displayed on the CRT. Visual display is extremely useful.

KUPATT

This program searches for the parameters of the Kubin-Kucera model which best fits the experimental pulse phase lag and amplitude ratio. The experimental phase lag and amplitude ratio may be input as data directly or it may be read from an input file (from 'pulse'). This program contains the pattern search logic. Some manipulation is required by the user to direct this portion of the program to search for particular variables, to input the starting values, to set step sizes, and to direct appropriate output. Note: in this project it was found essential to give very accurate starting values for the parameters which are contained in the first moment expression. As these parameters can be easily evaluated from the first moment so this presents no real problem.

KUBIN

This program calculates the Fourier coefficients of the Kubin-Kucera model given input values of the parameters. Using the Fourier coefficient expansion theorem, the pulse is then reconstructed in the time domain. The reconstructed pulse is then visually displayed and may be plotted on hard copy. This program is useful for testing the time fit of the experimental pulse with the model prediction using the parameters arrived at in 'KUPATT'.

AXPATT and AXDISP

These two programs are useful in testing the basis system operation using glass beads. These programs are based on a limiting case of the Kubin-Kucera model, that is, the axial dispersion model. They perform essentially the same functions as KUPATT and KUBIN.

2.3 PRELIMINARY RESULTS

Preliminary results will be presented of tests intended to verify the proposed method, to evaluate its potential use and limitations and to develop the computer programs needed. The two main sets of tests that will be described are: 1) tests of the trace of pulses passed through fresh and packed columns of well-characterized HDS catalysts, supplied by the U.S. DOE; and 2) tests of the pore structure of siderite, FeCO_3 which was decomposed to different extents and subsequently sintered.

2.3.1 Tests of the Pore Structure of Fresh and Aged (plugged) Catalysts

Three pairs of well-characterized fresh and aged catalysts were obtained from the U.S. DOE, PETC. The samples were packed in 40 cm 1/4" glass columns, degassed and tested using pulses of inert and active gases. The carrier was nitrogen. Figures 2.7 and 2.8 are pore structure data as obtained from DOE.* Figures 2.8 and 2.9 are the computer-transcribed versions of the DOE data for the fresh and aged Shell 324 and a DOE catalyst, RET 50570. The data show that the major change

*Courtesy of Dr. Richard Ticher.

POROSITY DETERMINATION

SAMPLE Shell 324 modified

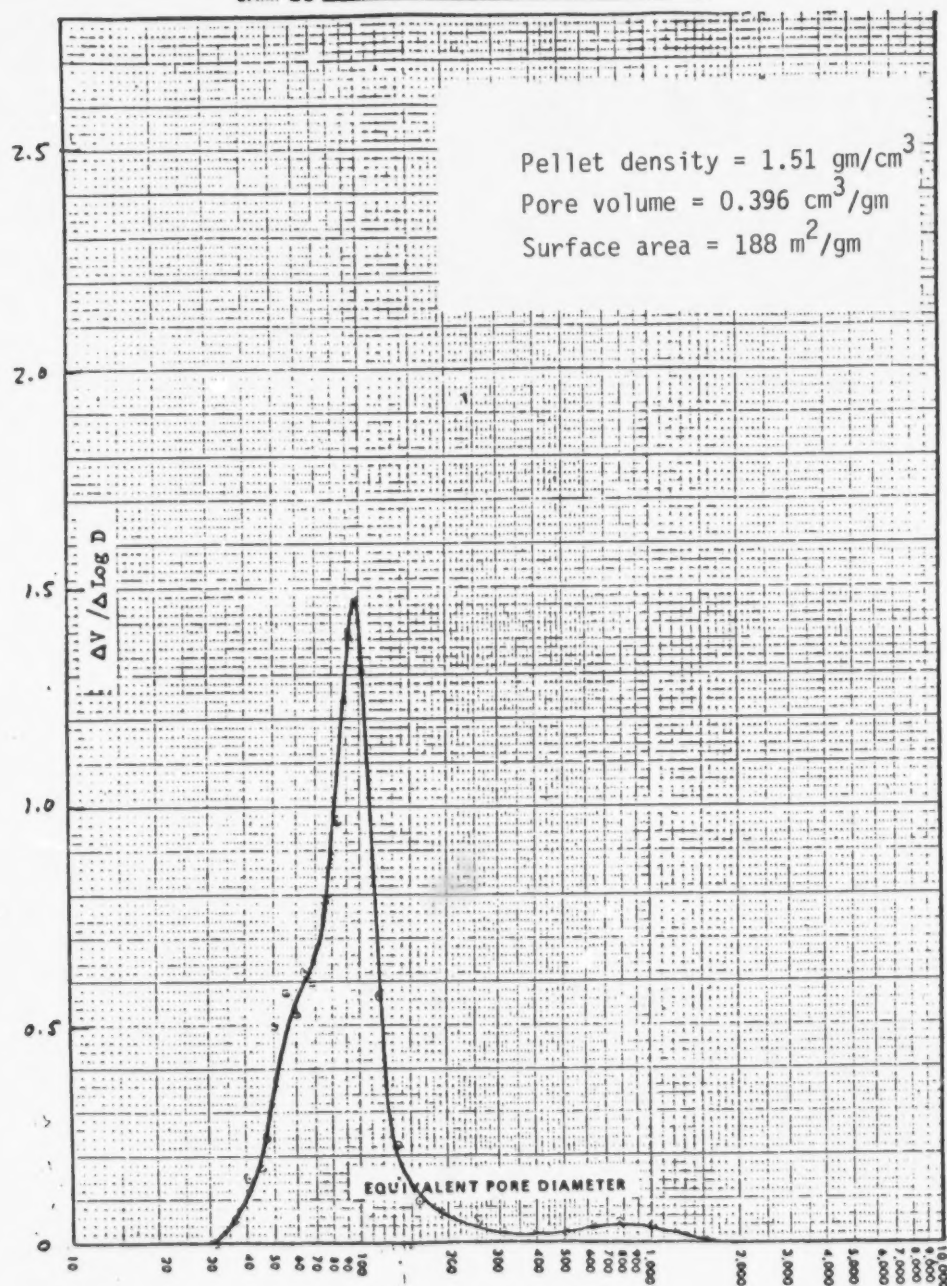


Figure 2.7 Pore structure of fresh Shell 324 catalyst

POROSITY DETERMINATION

SAMPLE LCR-17

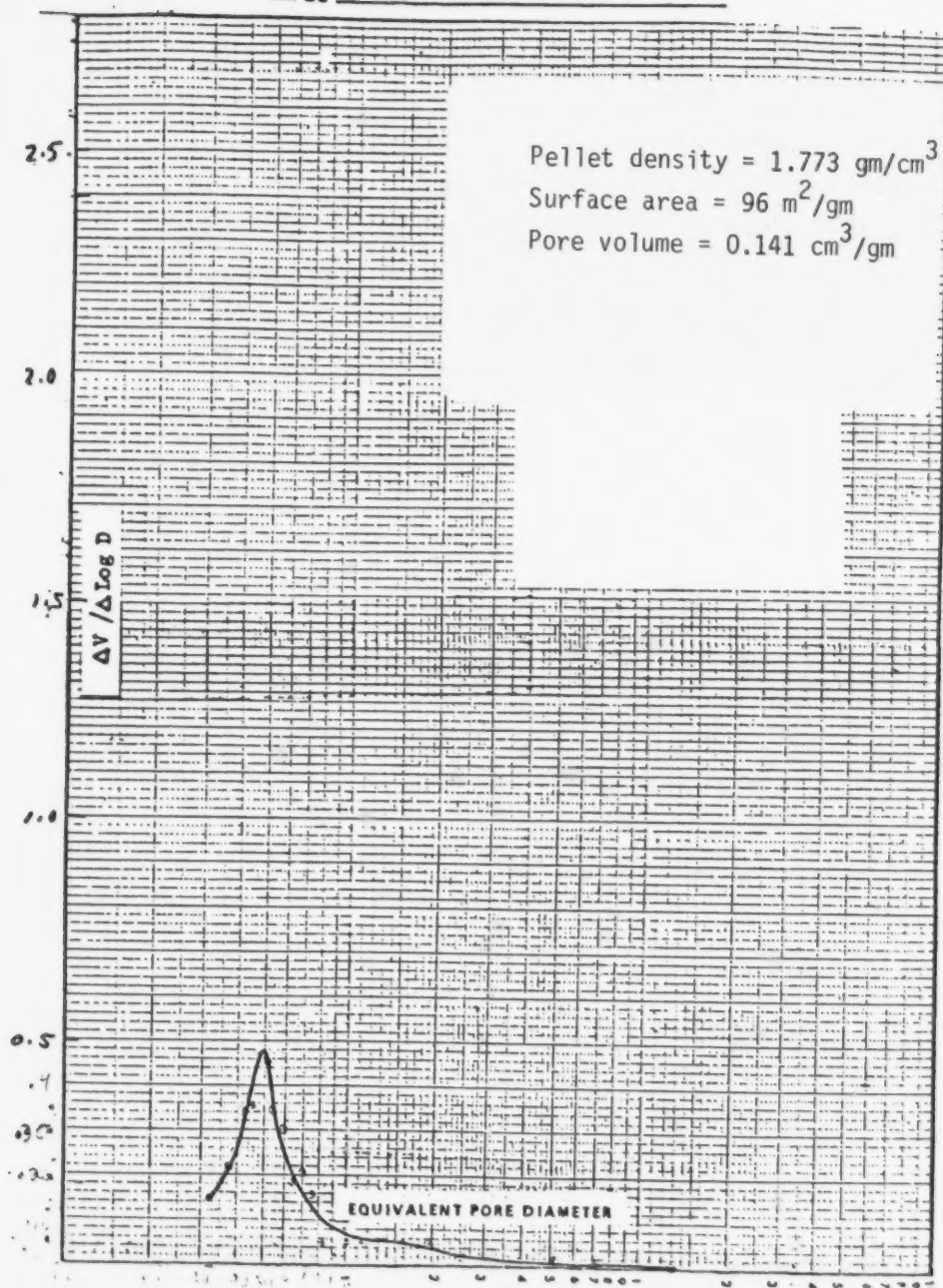
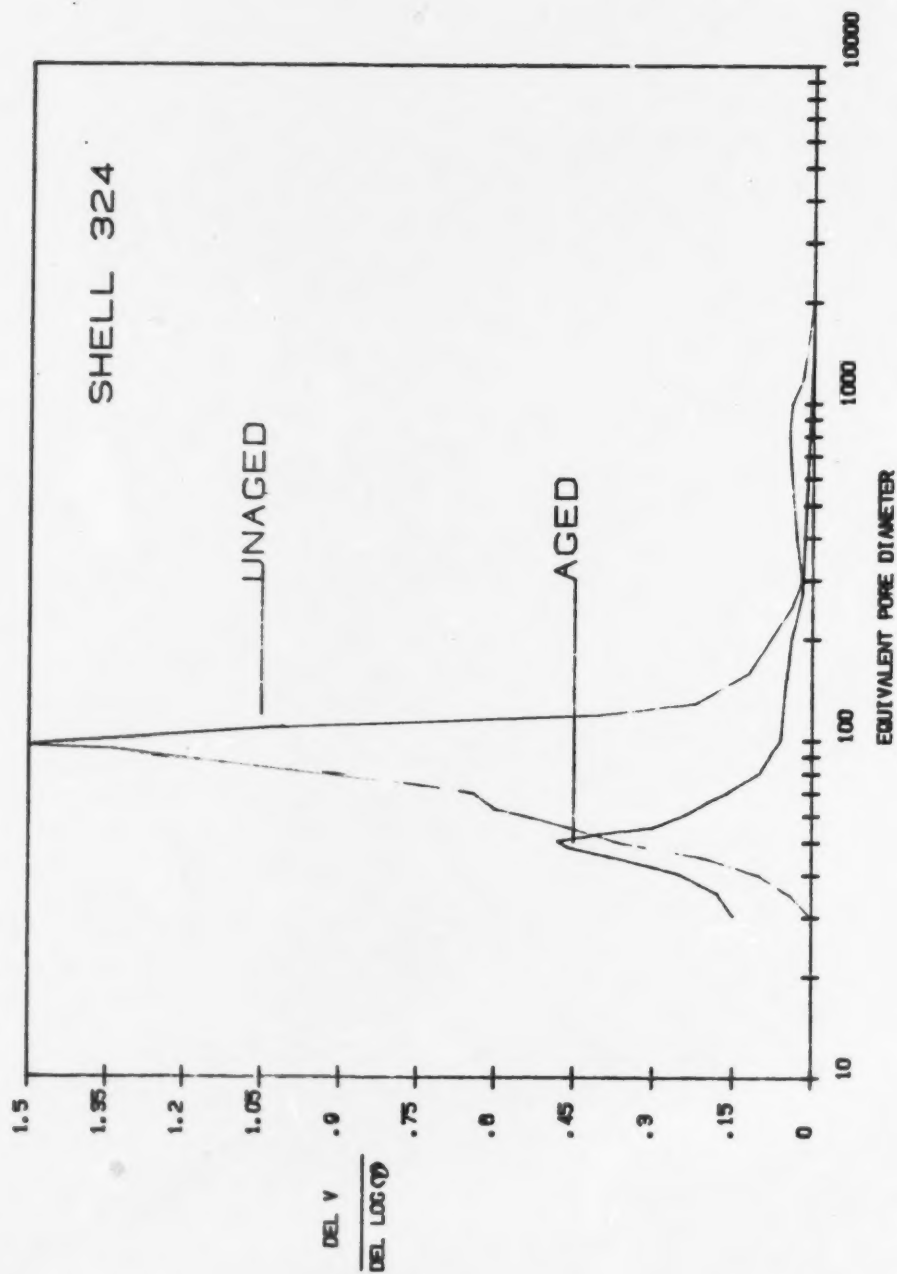
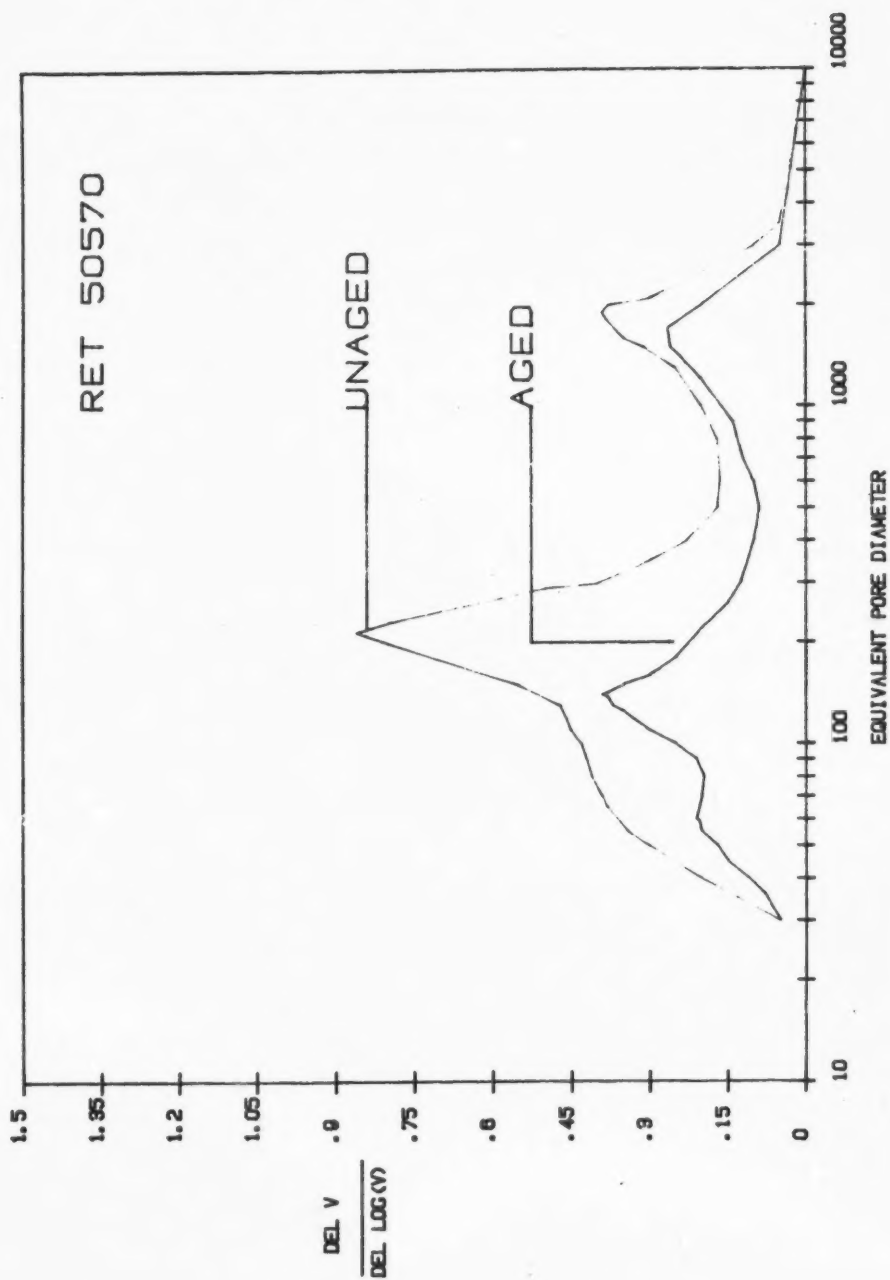


Figure 2.8 Pore structure of fouled Shell 324 catalyst



PORE SIZE DISTRIBUTION FOR AGED AND UNAGED CATALYST

Figure 2.9 Transcribed - DOE Pore Structure Data



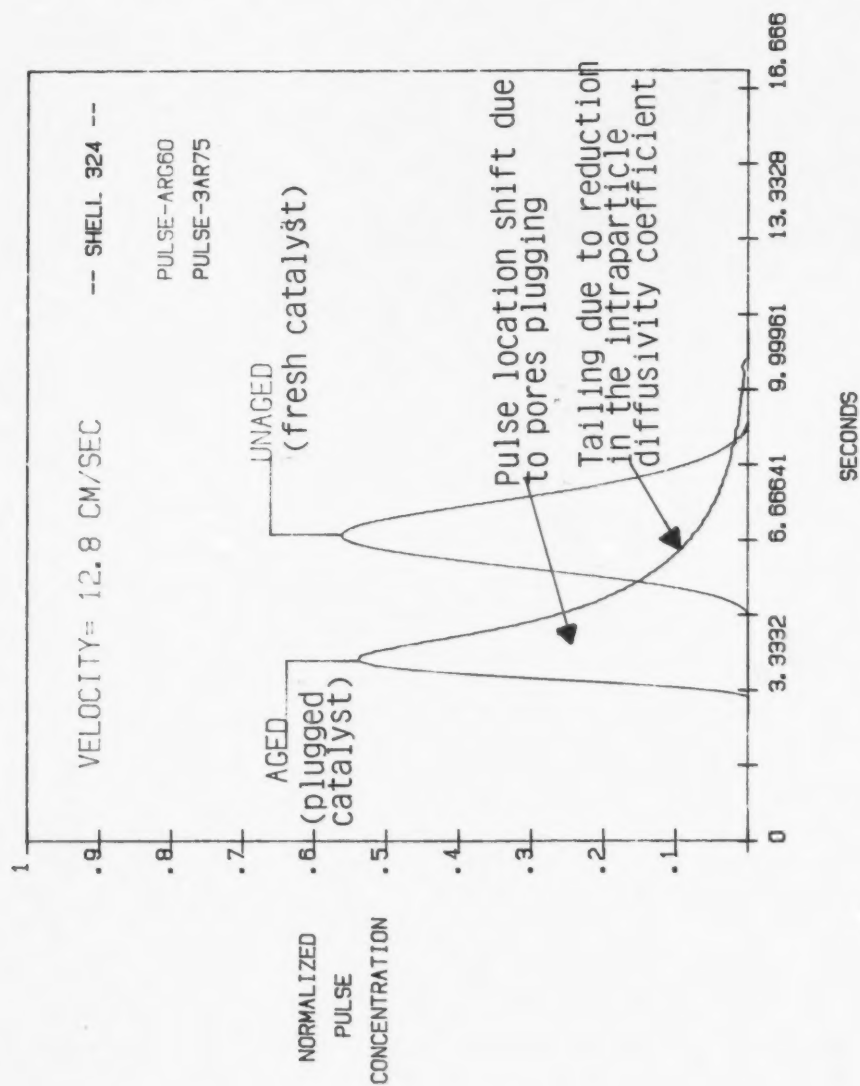
PORE SIZE DISTRIBUTION FOR AGED AND UNAGED CATALYST

Figure 2.10 Transcribed DOE Pore Structure, Catalyst RET 50570

in the pore structure was plugging or elimination of the pores around $100 \text{ \AA} - 180 \text{ \AA}$. Plugging of the pores reduces the porosity of the solid and causes the diffusivity coefficient of the gas to decrease. Figure 2.11 shows the normalized pulse tracer response of Argon pulses passed through columns of the fresh and the plugged Shell 324 catalyst. Plugging the pores caused the mean residence time of the pulse to shift from about 6 sec to about 4.2 sec. Moreover, the pulse passed through the column with the plugged catalyst, became skewed and tailing, mainly due to the reduction in the diffusivity. The intraparticle diffusivity coefficient decreased from about $3 \cdot 10^{-3} \text{ cm}^2/\text{sec}$ in the fresh catalyst to about $5 \cdot 10^{-5} \text{ cm}^2/\text{sec}$ in the plugged catalyst. The porosity of the original catalyst was 0.6 and of the plugged catalyst about 0.25.

The effect of changes in the pore structure are more visible when the carrier gas flows fast past the solid. Figure 2.12 shows the normalized pulses of Argon passed through the plugged Shell 324 column. When a superficial gas velocity of 22.8 cm/sec was used, a larger skewness was observed than when the velocity was 12.8 cm/sec. The calculated parameters of the solid are not sensitive to the gas velocity and/or the column temperature in a reasonable range of gas velocities; however, the sensitivity of the method depends on the solid particle size and the absolute magnitude of its porosity. The same phenomena that were observed with the Shell 324 catalyst were observed with the bimodal DOE catalyst 50570 as seen from Figure 2.13. Even at gas velocity of 8.9 cm/sec, the pulse passed through the aged catalyst appeared after a shorter period and was more skewed.

Several tests were conducted in order to determine the relative roles of physical and chemical adsorption. The essence of the tests involved the use of gases with different affinities to the solid surface in order to determine the nature of the surface interaction. The gases tested were Argon, Helium, methanol, dimethyl ether, pentane and benzene. To recognize cases where physical or chemical adsorption occurred, pulses of the same gas were injected at the same flow rate but at different column temperatures. Whenever chemical or physical adsorption occur, plotting $\log(t - t_0)$ vs. $1/T$ should yield a straight line with a slope



NORMALIZED PULSE CONCENTRATION VERSES TIME FOR AGED AND UNAGED CATALYST

Figure 2.11 Pulse of Ar through a fresh and a plugged catalyst

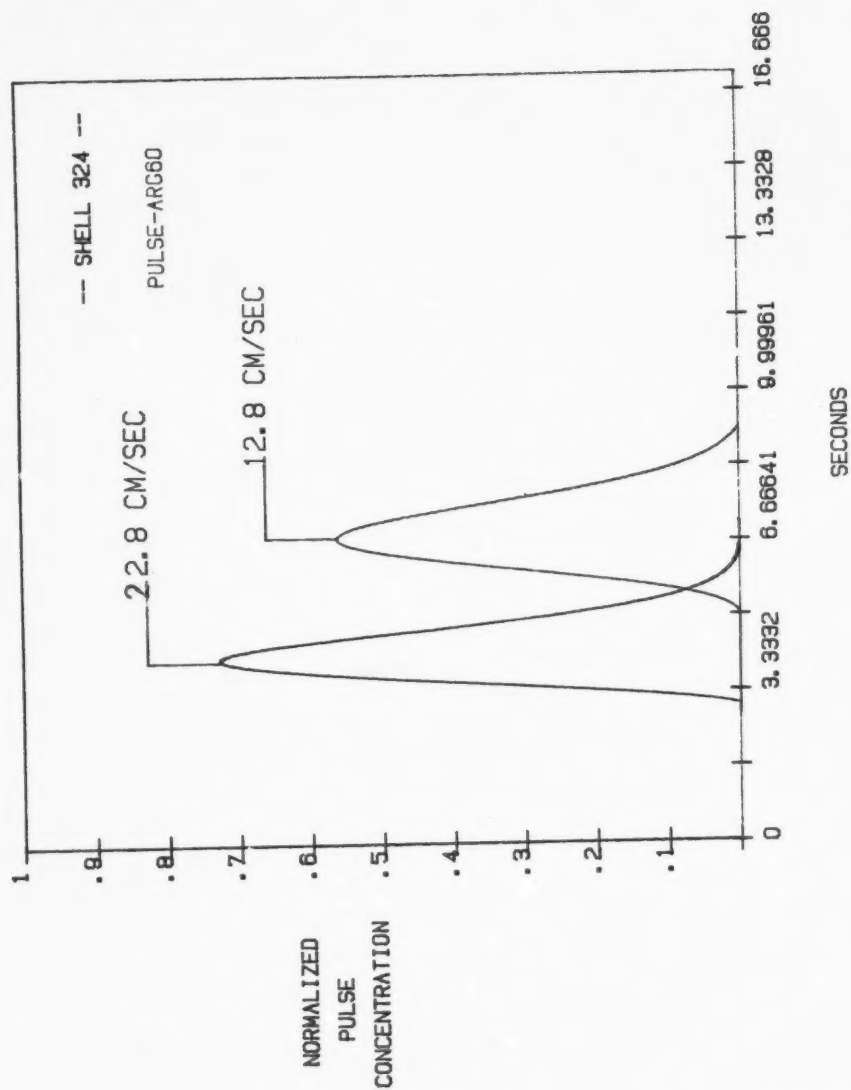


Figure 2.12
NORMALIZED PULSE CONCENTRATION VERSUS TIME FOR DIFFERENT FLOW RATES

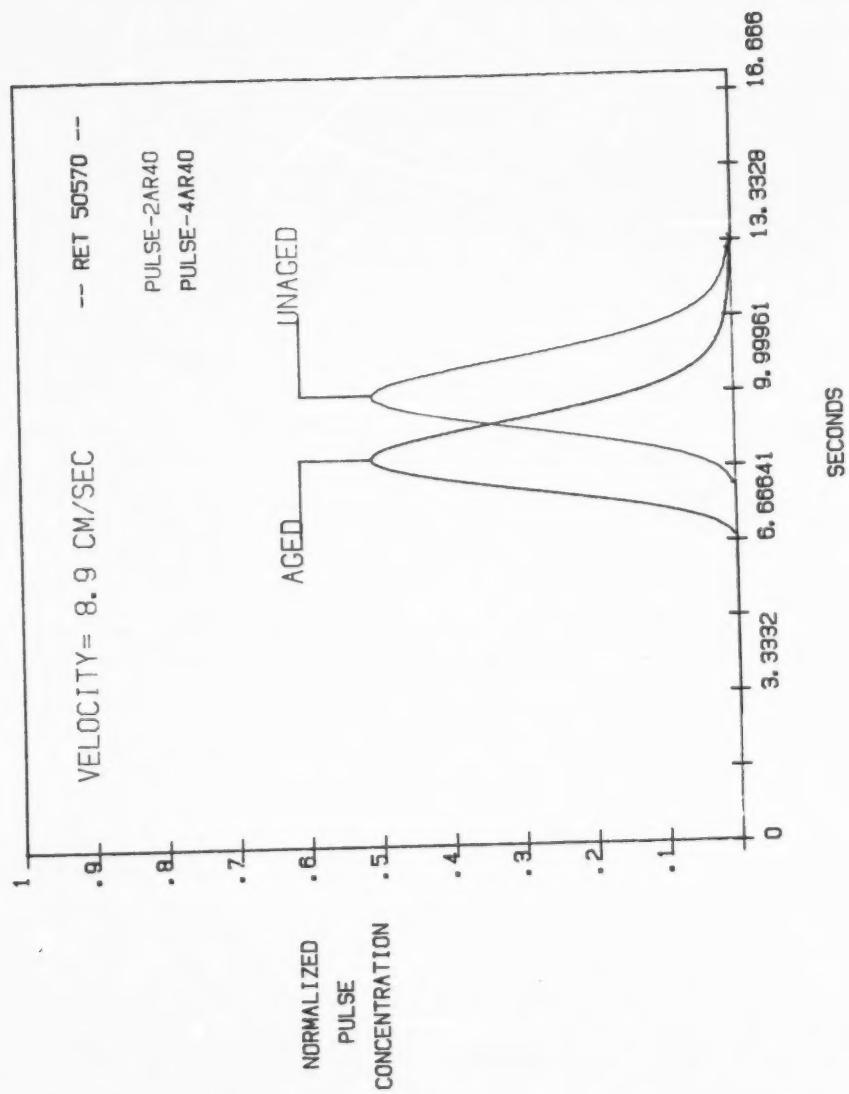


Figure 2.13
NORMALIZED PULSE CONCENTRATION VERSES TIME FOR AGED AND UNAGED CATALYST

of $-\Delta H/R$. If $\Delta H \sim 0$, no interaction occurs, if $2 < -\Delta H < 6$, physical adsorption occurs and if $12 < \Delta H$, chemical adsorption occurs. Note that t is the pulse residence time and t_0 the no-adsorbing gas residence time, calculated by dividing the void volume by the gas flow rate. Argon and Helium, as expected, appear not to adsorb to the surface in the temperature range of 30-200°C. However, gases like pentane (Figure 2.14) physisorb with $H = -3.2$ kcal/mole. Chemisorption in general changes the nature of the surface of the solid. Results of H_2S chemisorption on CaO and $CaCO_3$ will be presented in a later chapter.

2.3.2 Tests of the Porosity of Siderite

Iron carbonate (siderite), $FeCO_3$, decompose to iron oxide, FeO , and CO_2 in a manner analogous to $CaCO_3$ but at a lower temperature.



This reaction also involves a change in the molar volume, i.e., the molar volume of $FeCO_3$ is 30.5 ml/mole and of FeO is 12.6 ml/mole. Thus, a porous solid is formed initially which when heated to about 900°C begins to sinter rather rapidly. We have chosen $FeCO_3$ because it reacts in a very similar manner to $CaCO_3$ but at a lower temperature, since the high temperature furnace has not arrived yet. (The molar volume of $CaCO_3$ is about 34.5 ml/mole and of CaO is about 16.5 ml/mole.) A 60 cm x 1/4" column was packed with -60+120 mesh siderite and decomposed by heating it at 550°C-900°C for different periods of time. The original average packing density was calculated by weighing the empty and packed columns. The instantaneous porosity was calculated by weighing the partially pyrolyzed column and calculating the weight of CO_2 lost.

Pulses of Argon were used to estimate the instantaneous porosity of the solid according to the scheme outlined previously. The data are shown in Figure 2.15. The agreement is excellent which supports the potential use of the pulse technique for in-situ gas-solid reactions analysis.

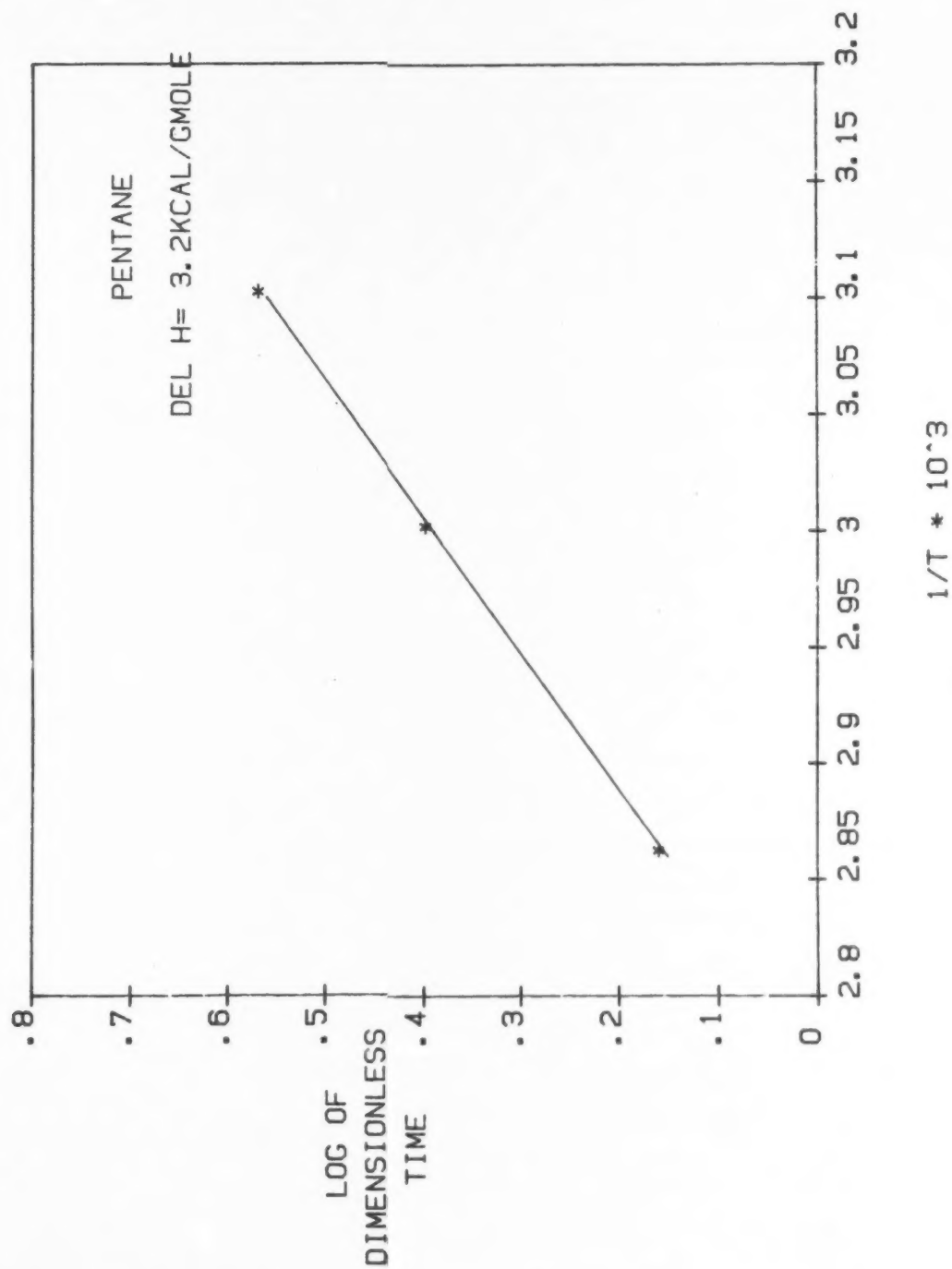


Figure 2.14

LOG OF DIMENSIONLESS MEAN RELATIVE RESIDENCE TIME VERSUS $1/T$

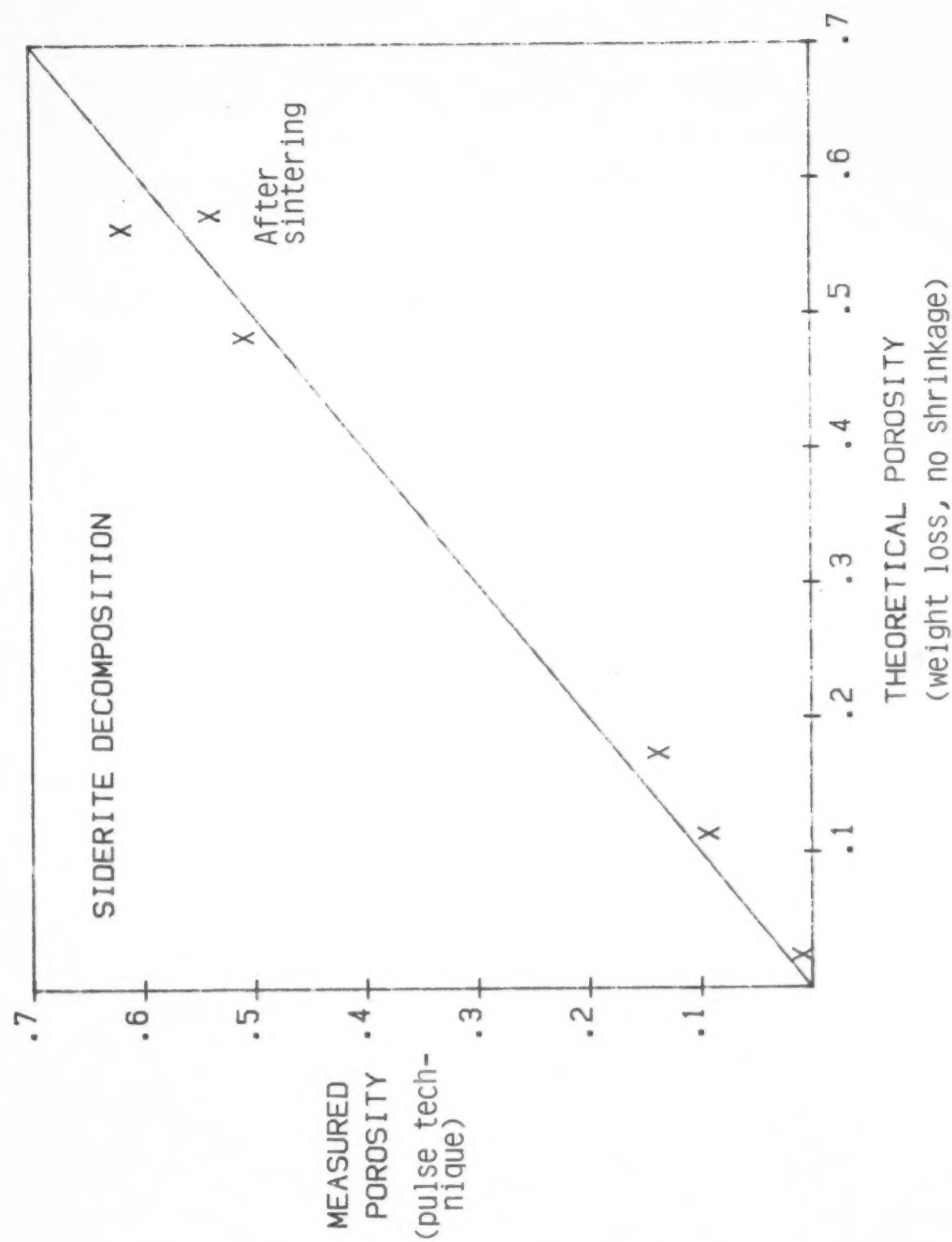


Fig. 2.15 MEASURED POROSITY BY PULSE ANALYSIS VERSUS THEORETICAL POROSITY CALCULATED FROM WEIGHT LOSS ANALYSIS

2.4 APPENDICES

2.4.1 Appendix A

The Fourier transform of $F(t)$ is given by:

$$\begin{aligned} F(i\omega) &= \int_0^{\infty} \text{EXP}(-i\omega t) * F(t) dt \\ &= \int_0^{2T} F(t) * \text{COS}(n\pi t/T) dt - i \int_0^{2T} F(t) * \text{SIN}(n\pi t/T) dt \\ &= T * b(n) - i T * a(n) \end{aligned}$$

Also,

$$F(t) = \sum_{n=1}^{\infty} a(n) * \text{SIN}(n\pi t/T) + \sum_{n=0}^{\infty} b(n) * \text{COS}(n\pi t/T)$$

Fourier Method Solution

Measurement of Adsorption on Porous Solids

In our last case we consider chromatographic measurement of adsorption and desorption rates as described by Schneider and Smith. The model for the chromatographic system, following Kubin and Kucera, is Equation (21) and Equation (22) modified by the addition of an adsorption term so

$$\frac{D_e}{\epsilon_p} \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{2}{r} \frac{\partial c_i}{\partial r} \right) - \frac{\rho_p}{\epsilon_p} \frac{\partial c_a}{\partial t} = \frac{\partial c_i}{\partial t} \quad (31)$$

and, assuming a linear isotherm,

$$\frac{\partial c_i}{\partial t} = k_a \left(c_i - \frac{c_a}{K_A} \right) \quad (32)$$

Boundary condition, in addition to Equation (23) is

$$\begin{aligned} c_a(r, 0) &= 0 \\ \bar{E}(i\omega) &= \exp \left[(\rho')^{1/2} - \sqrt{\rho' + i q' (1 + h(i\omega))} \right] \end{aligned}$$

where

$$\rho' = \left(\frac{U \epsilon L}{2D} \right)^2 \quad q' = \frac{\omega \epsilon D^2}{D}$$

$$h(i\omega) = \left[\frac{3k_f(1 - \epsilon)}{i\omega \epsilon R} \right]$$

and

$$\left[1 - \frac{\frac{D}{k_f} \frac{e}{\sqrt{\lambda}} \cosh(R\sqrt{\lambda}) + \frac{D}{Rk_f} \sinh(R\sqrt{\lambda})}{1 - \frac{D}{Rk_f} \sinh(R\sqrt{\lambda})} \right]$$

and $\lambda = \left(\frac{\epsilon p}{D_e} \right) i\omega$. Separating the transform of the response into real and imaginary parts, as in the simple dispersion case.

$$E(i\omega) = \exp \left[(\rho')^{1/2} - L \sqrt{\sigma} \cos \frac{\psi}{2} \right] \left[\cos \left(L \sqrt{\sigma} \sin \frac{\psi}{2} \right) - i \sin \left(L \sqrt{\sigma} \sin \frac{\psi}{2} \right) \right]$$

where

$$\sigma = \sqrt{\alpha^2 + \beta^2}, \quad \psi = \arctan(\beta/\alpha),$$

$$\lambda = \frac{\epsilon p}{D_e} \left[1 + \frac{\rho \epsilon p k_a k_A}{i\omega k_A + k_a} \right] (i\omega)$$

Equation (26) gives the transform as the sum of real and imaginary terms. The Fourier coefficients, the amplitude ratio and phase lag are expressed by Equations (29) and (30). The meaning of some of the terms, however, changes for this case.

$$\alpha = \left(\frac{\epsilon U}{2D} \right)^2 + \frac{3k_f(1 - \epsilon)}{RD}$$

$$\left[1 - \frac{X \cos M \sinh N + Y \sin M \cosh N}{X^2 - Y^2} \right] \quad (33a)$$

$$\beta = \frac{\omega \epsilon}{D} - \frac{3k_f(1 - \epsilon)}{RD} - \left[\frac{X \sin M \cosh N - Y \cos M \sin N}{X^2 + Y^2} \right] \quad (33b)$$

$$X = \frac{D_e}{k_f} \sqrt{\gamma} (\cos(\theta/2) \cos M \cosh N - \sin(\theta/2) \sin M \sinh N) + \left(1 - \frac{D_e}{k_1 R}\right) \cos M \sinh N \quad (34a)$$

$$Y = \frac{D_e}{k_f} \sqrt{\gamma} (\cos(\theta/2) \sin M \sin N + \sin(\theta/2) \cos M \cosh N) - \left(1 - \frac{D_e}{k_r R}\right) \sin M \cosh N \quad (34b)$$

where

$$M = R \sqrt{\gamma} \sin \theta/2, N = R \sqrt{\gamma} \cos \theta/2$$

and

$$\gamma = \sqrt{u^2 + w^2}, \quad \theta = \arctan(w/u)$$

$$w = \frac{\rho_p K_A^2 \omega^2 k_a}{D_e (k_a^2 + \omega^2 K_A^2)} = 0$$

$$u = \left[\frac{\epsilon_p}{D_e} + \frac{\rho_p K_A k_a}{D_e (k_a^2 + \omega^2 K_A^2)} \right]$$

Equations (25), (33) and (34) and the w, u contain the parameters of the chromatograph model, the properties D, D_e, k_f, K_A and k_a . These may be evaluated from A_n, φ_n for the chromatograph peak by a five dimensional search as previously described for the axial dispersion case.

$$D = E_A$$

$$D_e = D_c$$

2.4.2 Appendix B

Expressions Used in Parameter Estimation Search Technique:

$$A(n) = T * \text{SQR} (a(n)^2 + b(n)^2) \quad \text{'AMPLITUDE RATIO'}$$

$$\varphi(n) = \text{ARC TAN} (b(n)/a(n)) \quad \text{'PHASE LAG'}$$

Objective Function:

$$(\varphi(n) \text{ exp} - \varphi(n) \text{ model})^2 + (A(n) \text{ exp} - A(n) \text{ model})^2$$

2.5 NOTATION

- c = concentration of the adsorbable gas in the interparticle space, mole/ml
 c_i = concentration of the adsorbable gas in the pore space, mole/ml
 c_{ads} = concentration of the adsorbed gas per unit weight of adsorbent, mole/g
 c_0 = concentration of the adsorbable gas in the input concentration function, mole/ml
 D_e = effective intraparticle diffusion coefficient defined as the ratio of the diffusional flux through unit area of the geometrical surface of the particle to the negative of the intraparticle concentration gradient, sq. cm/sec.
 D_{AB} = binary molecular diffusivity, sq. cm/sec
 D_K = Knudsen diffusivity, sq. cm/sec
 E_A = effective axial dispersion coefficient, defined as the ratio of the axial diffusional flux through unit area of the total cross section of the column to the negative of the interparticle concentration gradient sq. cm/sec.
 k_{ads} = adsorption rate constant, defined by Equation (2.9), ml/g.sec
 k_f = mass transfer coefficient defined by Equation (2.10), cm/sec.
 K_A = adsorption equilibrium constant (adsorption coefficient), defined as $(c_{ads}/c)_{equil.}$, ml/g
 $m_n (n=0,1,2,..)$ = integrals, Equation (2.16)
 M = molecular weight of the diffusing substance, g/mole
 p = variable in the Laplace transformation
 r = length coordinate in the spherical particle of absorbent, measured from the center of particle, cm
 $\bar{r}$ = average radius of the pores, cm

- R = radius of the spherical particle of adsorbent, cm
 R_g = gas constant
 t = time, sec
 t_o = time necessary for saturation of the adsorbent in the bed under conditions of no resistance, sec.
 $t_{oA}, (t_o)_{inert}$ = time of duration of the injection of the adsorbable or inert gas in chromatography, sec.
 T = absolute temperature, °K
 v = linear velocity of the carrier gas in the interparticle space, cm/min
 z = length coordinate of the bed of adsorbent, measured from the inlet side, cm.

2.6 GREEK LETTERS

- α, E = interparticle void fraction in the adsorbent bed
 β, ϵ_p = intraparticle void fraction (internal porosity) of the adsorbent
 $\delta_0, \delta_1, \delta_2$ = expressions defined by Equations (2.21), (2.22), (2.23)
 μ_n', μ_n = n-th absolute and central moment of the chromatographic curve, respectively, Equations (2.15), (2.17)
 ρ_p = apparent particle density, g/ml

CHAPTER 3
IN SITU MONITORING OF SURFACE AREA TRANSFORMATIONS
DURING SINTERING OF CALCITE CALCINES
USING PULSED GAS CHROMATOGRAPHY

3.1 INTRODUCTION

It is generally accepted that the driving force of sintering can be related to the excess surface-free energy of the system. During sintering the intrapellet grains or pores may change shape in order to reduce the free energy of the system. Adjacent grains may form interconnecting necks which substitute high-energy free surface for lower energy grain boundaries. In some cases, where grain boundary or volume diffusion prevail, significant solid densification may occur.

Sintering is encountered in numerous process applications which utilize catalytic or reactive solids containing small pores, grains or dispersed phase distributions. The reduction of surface area which typically accompanies the sintering process often adversely affects the role and performance of these solids. Since the reactivity of a solid depends on the pore structure, free surface and grain morphology, there is a need for understanding the sintering behavior of specific solid systems in process applications.

In particular, there exists a sustained interest in the application of lime for high-temperature removal of sulfur-containing gases in the product and flue gas streams of coal gasifiers and coal-fired boilers. In these systems, calcium carbonate may be injected into pulverized fuel burners or introduced into a fluidized or fixed-bed arrangement. The basic reaction scheme common to each of these applications involves calcination of the carbonate to the oxide followed by sorption of the sulfur-containing species. The process of sintering occurs to a greater or lesser extent during each phase of this reaction scheme.

The effect of sintering may influence the fundamental morphology of the solid structure. A number of investigators have reported on the predominant role that solid structure plays in SO_2 -lime reaction (Bhatia and Perlmutter, 1961; Hartman et al., 1978; Borgwardt and Harvey, 1972).

It is now believed (to be published) that the sintering of lime, as it is formed from limestone, occurs in two distinct kinetic steps, with two very different kinetics. Initially very high surface area material is formed which rapidly sinters to a lower surface area material or what we commonly encounter as lime. The high surface area lime may have $20\text{--}65 \text{ m}^2/\text{gm}$ surface area and may survive 1-5 sec or less at 1000°C . The rapid, first-stage sintering kinetics are probably associated with highly mobile atomic species existing in the metastable structures which are formed during rapid decomposition. Because of the brief life time of this "active lime," high surface area limes are only observed for small particle calcines where the time scale for decomposition is commensurate with that of the first-stage sintering kinetics. For the large particle sizes investigated in this study, the time scale for complete decomposition is much greater than that of the first stage kinetics. Surface areas resulting from the relatively slow decomposition of large particles are typically found in the range of $.1\text{--}15 \text{ m}^2/\text{g}$. The second-stage sintering processes which are operative in these calcines occurs with a time scale of the order of minutes or hours. The low surface area material may have $0.1\text{--}5 \text{ m}^2/\text{gm}$ and will decay at 1000°C with timescale of the order of hours.

In this investigation, a method for continuously monitoring changes in pore structure in situ and at reaction conditions using pulsed-gas chromatography is described along with results on the calcite-lime system. Specific results pertaining to the solid structure modifying process referred to as sintering are discussed. The relative surface area is the structure-related variable which is continuously monitored in these experiments. All results pertain to the time dependence of the relative surface area, $S_g(t)/S_g(t_0)$, for the calcite-lime system.

The potential benefits that the pulsed-gas chromatographic method presents relative to more conventional structure measurement techniques (mercury penetration, inert gas adsorption-desorption, BET) include 1) facilitation of in situ analysis, 2) measurements are made at reaction conditions rather than at cryogenic temperatures or high pressures, 3) a single sample can be monitored throughout the course of transformation without disruption.

3.2 PULSED-GAS CHROMATOGRAPHY

Pulsed-gas chromatography (PGC) has been previously applied at relatively low temperatures to measure the transport and adsorption characteristics in catalysts and other solids (Hsu and Haynes, 1981; Chihara et al., 1978; Scott et al., 1974). A few studies have been published concerning the use of PGC to evaluate the effect of pore structure transformation (fouling, gasification) on transport and adsorption properties (Debelock et al., 1982; Chou and Hegedus, 1978; Butt et al., 1975). However, these studies were not conducted in situ or at reaction conditions.

In the PGC procedure, a pulse of tracer gas is introduced at the entrance of a column packed with a porous solid. The input tracer pulse is conveyed through the column by means of a flowing carrier gas. During its journey through the column, the tracer pulse interacts with the solid structure in some manner, resulting in a characteristic residence time distribution, i.e., the shape of the pulse contains information on the solid surface. A suitable detector located at the column exit is used to monitor the residence time distribution of the tracer.

A theoretical model that describes the pulse shape in terms of well-defined interaction processes is used to deduce information on the solid structure from the pulse shape. For an adsorbable tracer, it is evident that the surface area of a porous solid will have a significant impact on the specific interaction behavior of a particular tracer-solid system. The purpose of this paper is to elucidate how features of the pulse residence time distribution can be directly

related to the surface area of a porous solid using the PGC approach and to present information on the kinetics of the second-stage sintering of lime.

Several investigators have reported that the decomposition of carbonates is described by a shrinking core model (Gallagher and Johnson, 1976; Hills, 1968). Even upon complete decomposition, it is possible and perhaps probable that the resulting pore structure of the product oxide varies in the radial dimension of the pellet. Since the PGC method is dynamic in nature, that is, the tracer gas may probe various depths of the pellet, it is important to evaluate the effects of radial non-uniformities on pulse dispersion. The PGC model described in this paper is similar in form to the model of Schneider and Smith (1968), which is based on the developments of Kubin (1965) and Kucera (1965). The model described here differs from that of Schneider and Smith primarily in that the pellet is assumed to possess radially varying transport and pore structure properties. Also, some aspects of the notation have been altered such as the separation of the equilibrium adsorption constant into a specific surface area component, S_v , and a structure-independent adsorption constant, K_a , defined on a per-unit surface area basis.

3.3 THEORY

A model is described for the dispersion of an adsorbable tracer in a packed column containing porous pellets of arbitrary geometry. The local effective diffusivity coefficient, porosity and surface area per unit volume pellet are assumed to be variable throughout the dimension of the pellet. The concentration, $C(z,t)$, of an adsorbable tracer as a function of time and axial column position is obtained from solution of the following material balance equations.

The mass balance for tracer material in the inter-pellet volume is given by:

$$\begin{aligned} (D_a/E) \partial^2 C / \partial z^2 - (V/E) \partial C / \partial z - \partial C / \partial t \\ - w(1-E)(D_{e,N}/RE) (\partial C_{i,N} / \partial r)_{r=R} = 0 \end{aligned} \quad (3-1)$$

where D_a is the effective axial dispersion coefficient; E is the column voidage; V is the superficial velocity; $D_{e,N}$ is the effective diffusivity in the outermost zone (Nth); w is a geometric factor equal to three, two or one for a sphere, semi-infinite cylinder or slab, respectively; R is the characteristic pellet radius or half-width.

The pellet is assumed to be comprised of the multi-zoned structure shown in Figure 3.1. The effective diffusivity, porosity and surface area per unit volume are constant within a single zone. The dimension of each zone may be taken to be as arbitrarily small as desired. The mass balance for each zone, n , is given as:

$$(D_{e,n}/\beta_n)(1/r^{w-1}) \partial/\partial r (r^{w-1} \partial C_{i,n}/\partial r) - \partial C_{i,n}/\partial t - (S_{v,n}/\beta_n) \partial C_{a,n}/\partial t = 0 \quad (3-2)$$

where $C_{i,n}$ is the concentration of tracer in the pore volume of the n^{th} zone; $C_{a,n}$ is the concentration of tracer adsorbed on the pore walls of the n^{th} zone and has units of mole/cm²; $S_{v,n}$ is the local, volume specific surface area, and β_n is the local porosity.

Adsorption in each zone is assumed to be linear:

$$\partial C_{a,n}/\partial t = k_a (C_{i,n} - C_{a,n}/K_a) \quad (3-3)$$

where k_a is the adsorption rate constant having units cm/sec and K_a , the adsorption equilibrium constant, is given by:

$$K_a = (C_{a,n})_{\text{eq}}/C_{i,n} \quad (3-4)$$

The initial conditions are given by:

$$C = C_{i,n} = C_{a,n} = 0 \quad z > 0, \quad t = 0 \quad (3-5)$$

The boundary conditions at the junction between each adjacent zone is given by:

$$C_n = C_{n+1} \quad r = r_n \quad (3-6)$$

$$D_{e,n}(\partial C_{i,n}/\partial r) = D_{e,n+1}(\partial C_{i,n+1}/\partial r) \quad r = r_n \quad (3-7)$$

for $n = 1, 2, \dots, N-1$

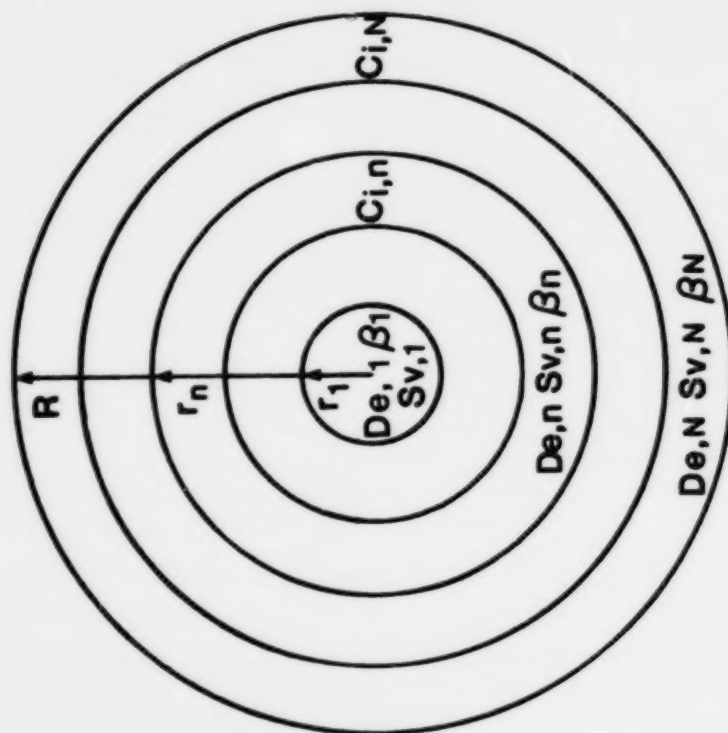


Figure 3.1 Multi-zoned pellet with radially varying transport and pore properties

For zone one, the symmetry condition requires:

$$(\partial C_{i,1}/\partial r)_{r=0} = 0 \quad (3-8)$$

The external boundary condition for the pellet is:

$$D_{e,N}(\partial C_{i,N}/\partial r)_{r=R} = k_f(C - (C_{i,N})_{r=R}) \quad (3-9)$$

The boundary conditions for the mobile phase are given by:

$$C = C_p(t) \quad z = 0 \quad (3-10)$$

where $C_p(t)$ is the time-dependent tracer concentration which exits the preheat column and enters the packed bed, and $C(z,t)$ is bounded for all z .

3.4 FIRST ABSOLUTE MOMENT

The first absolute moment of the pulse residence time distribution is defined as:

$$\mu_1^i(z) = \int_0^\infty t C(z,t) dt / \int_0^\infty C(z,t) dt \quad (3-11)$$

Solution of equations 3-1 to 3-10 results in the following expression for the first absolute moment evaluated at $z = L$ (see Appendix):

$$\mu_1^i(L) = (L/V)(E + (1-E) \bar{\beta} + K_a(1-E) \bar{S}_v) + \mu_{1,p}^i \quad (3-12)$$

where,

$\mu_{1,p}^i$ = mean residence time in preheat section

$$\bar{\beta} = \sum_{n=1}^N \beta_n v_n = \text{average pellet porosity} \quad (3-13)$$

$$\bar{S}_v = \sum_{n=1}^N S_{v,n} v_n = \text{average surface area per unit pellet volume} \quad (3-14)$$

$$v_n = (r_n^W - r_{n-1}^W)/R^W = \text{volume fraction of } n^{\text{th}} \text{ zone} \quad (3-15)$$

Equation 3-12 is shown to be independent of particle radius, transport and rate parameters. Furthermore, equation 3-12 expresses the somewhat surprising result that the first absolute moment of an

adsorbable tracer depends only on the volume-averaged properties, $\bar{\beta}$ and $\bar{S}_v$ and not on the specific radial distribution of these quantities. This result provides the fundamental basis for relating the relative surface area information derived from the dynamic pulse method to the averaged surface measure provided by BET methods.

It should be noted that, while the first moment provides pellet-averaged properties, the detailed pulse shape contains more refined information concerning the radial distribution of properties (see Chou and Hegedus, 1978). However, the ability to extract this information is probably severely limited due to the coupled nature of the process coefficients.

3.5 CALCULATIONS

The time delay of the first absolute moment of an adsorbable tracer (CO_2) relative to that of a nonadsorbable tracer (N_2), denoted by $\Delta\mu_1'$, is given as:

$$\Delta\mu_1' = (L/V) K_a (1-E) \bar{S}_v \quad (3-16)$$

$$= A \bar{S}_g \quad (3-17)$$

where,

$$A = (L/V) K_a \rho_c \quad (3-18)$$

and ρ_c is the apparent column-packing density with units (g solid/column volume).

Since mass is conserved during sintering, A is a time-independent constant for isothermal conditions. The relative surface area, S_r , defined as the ratio of specific surface area, S_g , at time t relative to any reference time t_0 is given by:

$$S_r(t) = S_g(t)/S_g(t_0) = \Delta\mu_1'(t)/\Delta\mu_1'(t_0) \quad (3-19)$$

Equation 3-19 gives an expression for determining the temporal variation in relative surface area from the pulse residence time distribution for an adsorbable/nonadsorbable tracer pair.

During densification which typically accompanies later stages of sintering, pore space may become isolated from the bulk of the interconnecting pore network and thus unavailable to the tracer probe. The volume of pore space per gram of solid which becomes occluded, v_o , relative to time t_o , is given by:

$$v_o = (V/L) (\mu_{1,\text{non}}^i(t_o) - \mu_{1,\text{non}}^i(t))/\rho_c \quad (3-20)$$

In the experimental system used in this study, the measured first absolute moments for adsorbable and nonadsorbable tracers contain a time lag due to the existence of extra column volume in the preheat and post-cooling sections. In theory, the time lag for the nonadsorbable tracer may not be identical to that of the adsorbable tracer due to the presence of axial temperature and velocity gradients in the extra column volume sections. It is expected that the difference in time lags would diminish with increasing Peclet number. The difference in time lag for the two pulses was evaluated at typical operating velocities and temperatures using an empty column. The mean residence times for the two pulses varied by less than one second (22.8 sec for CO_2 vs 22.0 for N_2). Since the mean residence time for CO_2 in a packed column arrangement was typically on the order of 100 seconds, this discrepancy can be ignored for calculation purposes.

3.6 EXPERIMENTAL

A schematic of the apparatus is shown in Figure 3-2. The flow of helium carrier gas (CG1) through the primary and reference column is regulated by needle valves NV1 and NV2. Column head pressure is monitored at P1 and P2. The pressure drop through the column is typically less than 2 psi. A prepared mixture of 5-10% CO_2 in He is stored in sample piston, PS1. The tracer mixture is directed through an 8-port injection valve containing a 50- μL sample loop. N_2 pulses are generated by directing pure N_2 from tank T1 through the injector valve.

The reactor and reference column (packed with precalcined pellets) are contained in a rheostat-controlled, high-temperature furnace. Upon exiting the injector valve, carrier gas is preheated to sintering

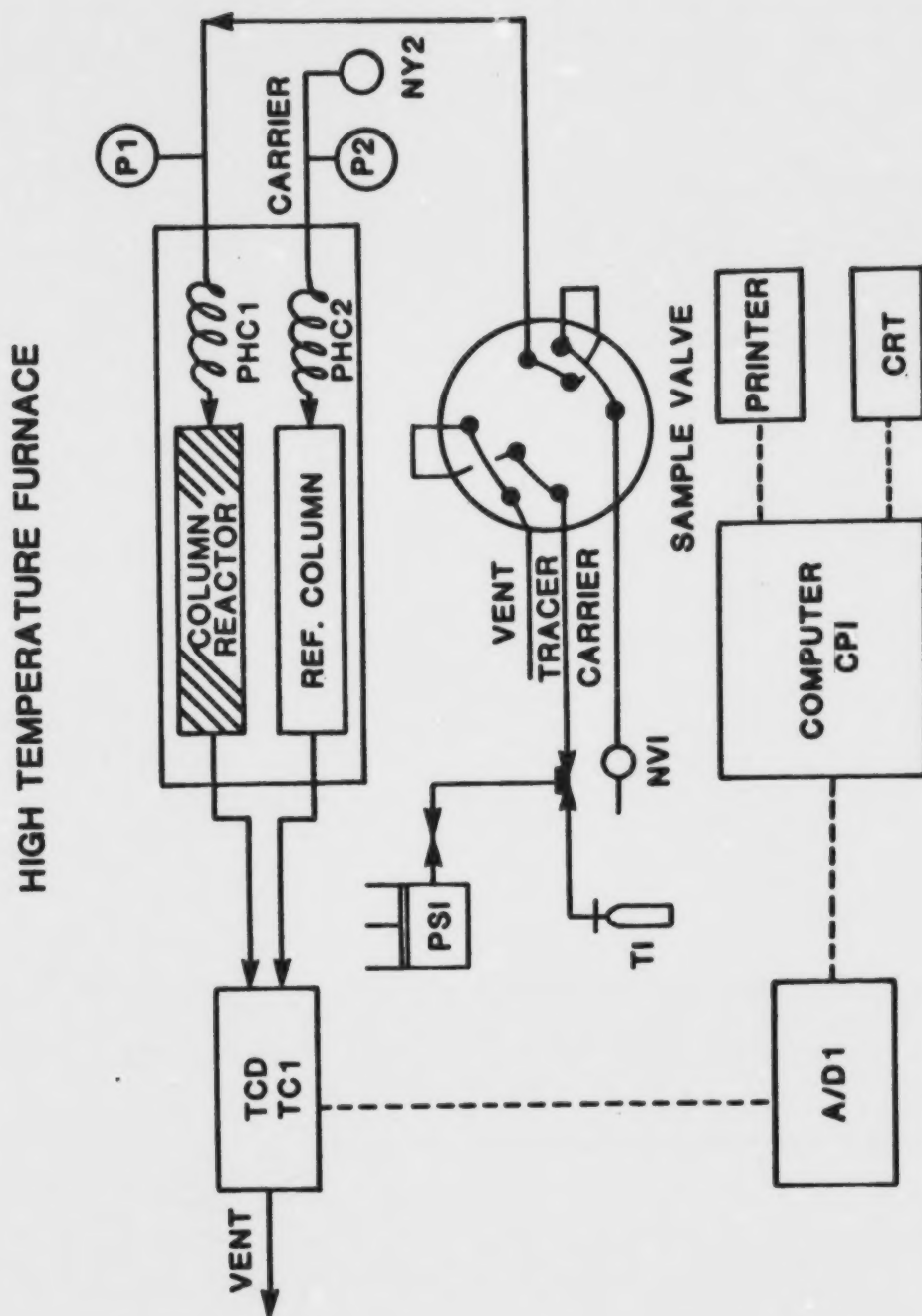


Figure 3.2 Flow scheme and configuration options for pulse apparatus

temperature in preheat coils, PHC1 and PHC2. The outlet concentration from the columns is monitored by a thermal conductivity detector, TC1. The analog TCD signal is converted to digital form by AD1 under computer direction, CP1. The digital data are stored in the computer workspace (Digital Corp. MINC 11) for further processing and on diskette for permanent record. The frequency of digitization is varied in order to define the output pulse by a minimum of approximately 100 points.

The column reactor is a 1/4" OD, 25 cm long S.S. tube which is packed with calcite, a relatively pure crystalline calcium carbonate. Runs were made with size fractions of 12/20 and 20/35 mesh. Various heating rates were imposed on the samples in order to bring the furnace to the desired isothermal sintering temperature. Above 800°C, typical heating rates were in the range of 1-3°C/min, but were not precisely controlled. Decomposition of the calcite is observed to proceed at accelerated rates as furnace temperature approached 830-850°C. The first pulse series is introduced into the column upon complete decomposition as signaled by detector stabilization. Detector stabilization generally is achieved one to two hours after the onset of rapid decomposition.

Immediately following complete decomposition, the initial BET surface areas of the calcines are in the range of about 5-15 m²/g. The variation of initial surface area for these samples indicates a relatively sensitive dependence on heating rate.

3.7 RESULTS

Figure 3-3 shows the resulting CO₂ tracer residence time distributions as a function of sintering time for a typical run. As time progresses and surface area diminishes, the pulses are observed to have reduced elution times and pulse widths.

3.7.1 Correlation of $\Delta\mu_1^i$ AND BET SURFACE AREA

As previously shown in equation 3-17, $\Delta\mu_1^i$ is in theory directly proportional to S_g for given column conditions and temperatures assuming that chemisorption of CO₂ is linear. To test for adsorption linearity,

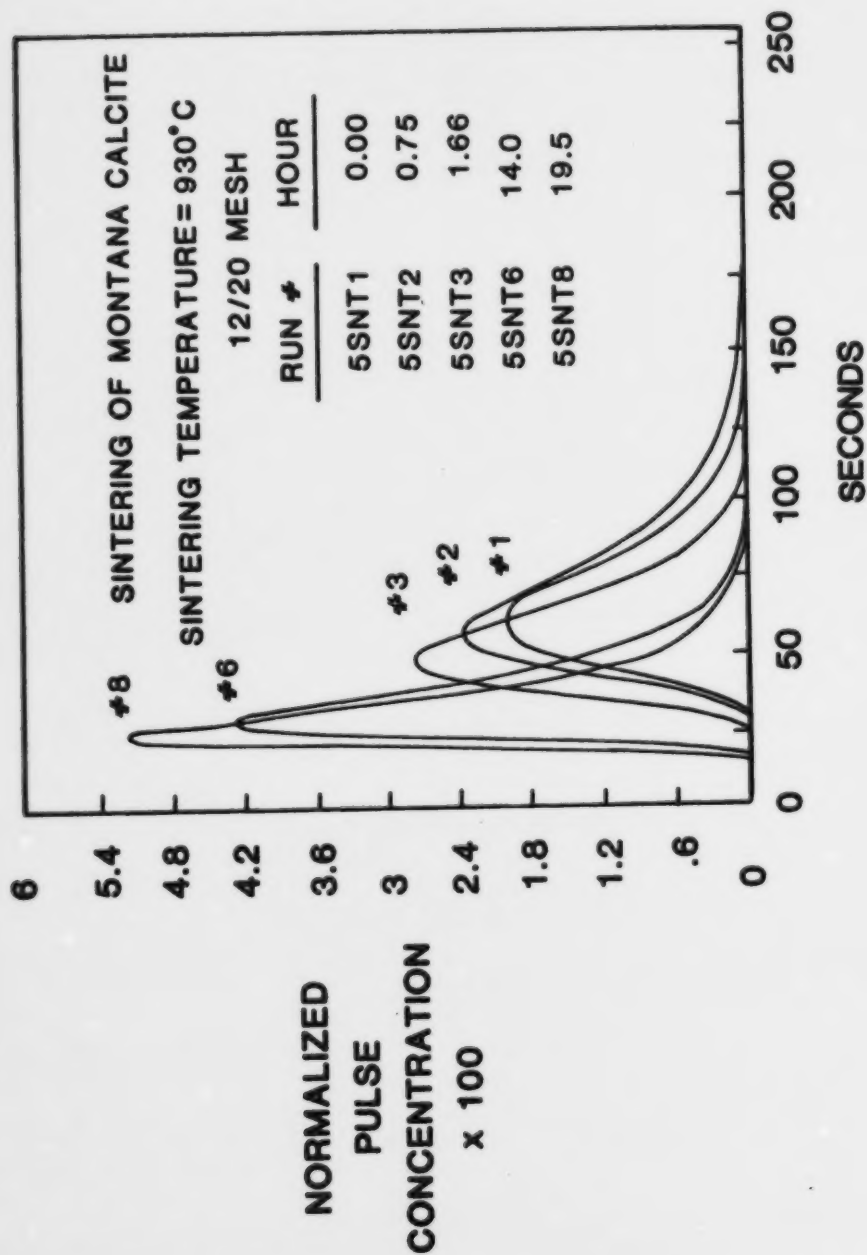


Figure 3.3 Normalized tracer response of CO₂ on calcines from Montana calcite

a series of CO_2 dilutions were prepared and injected into a column containing a calcined sample at 900°C . An increase in mean residence time of about 10% was recorded for a 10% mixture compared to that of pure CO_2 . Below concentrations of 10% for the inlet pulse, virtually no changes in mean residence time or pulse shape as determined from Fourier analysis was observed. It should be noted that, due to dispersion in the preheat column, the actual concentration of the tracer at the packed column entrance is substantially less than that of the mixture in the sample loop. All measurements were conducted in the apparently linear adsorption region of 5-10% CO_2 in He.

In order to verify that $\Delta\mu_1^i$ is proportional to S_g , as determined by BET analysis, a number of sintering runs were performed and terminated at various values of $\Delta\mu_1^i$. For each of these runs, $\Delta\mu_1^i$ is measured at 930°C . A plot of $\Delta\mu_1^i$ vs BET surface area is shown in Figure 3.4. The resulting linear relation confirms the assertions of equation 3-17. From the slope of this curve, a value of K_a at 930°C is calculated to be 1.76×10^{-4} (mole/cm²)/(mole/cc).

Figure 3.5 shows a plot of $\Delta\mu_1^i$ vs reciprocal temperature for various calcines of differing specific surface area. The temperature is programmed in a time scale small compared to that of sintering for these measurements. Based on the slope of the plot, a value of approximately -37 kcal/gmole is calculated for the heat of chemisorption of CO_2 on the calcine product.

3.7.2 Time Dependence of Sintering

A reduction in surface area may result from a number of fundamental transport mechanisms including evaporation-condensation, bulk, surface, or grain boundary diffusion. The sintering process is generally considered to occur in defined stages; initial, intermediate and final. The initial stage involves contact and neck formation between adjacent grains (German and Munir, 1975a, 1975b; Kuczynski, 1949). The intermediate stage involves further coalescence and densification resulting in the eventual isolation of pores (Nichols, 1966; Coble, 1960). The nature of sintering in the intermediate stage depends on critical

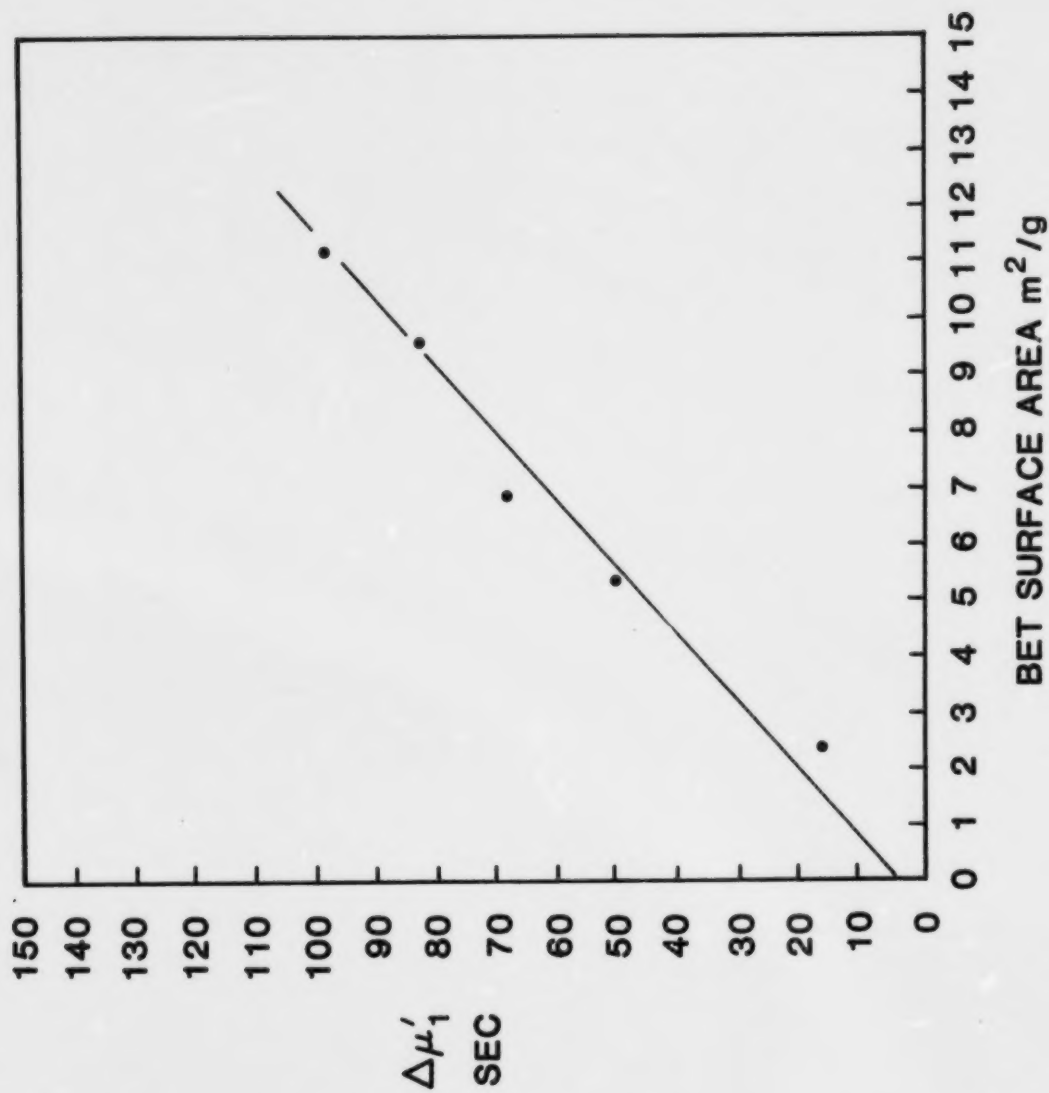


Figure 3.4 The dependence of the incremental first moment on the surface area

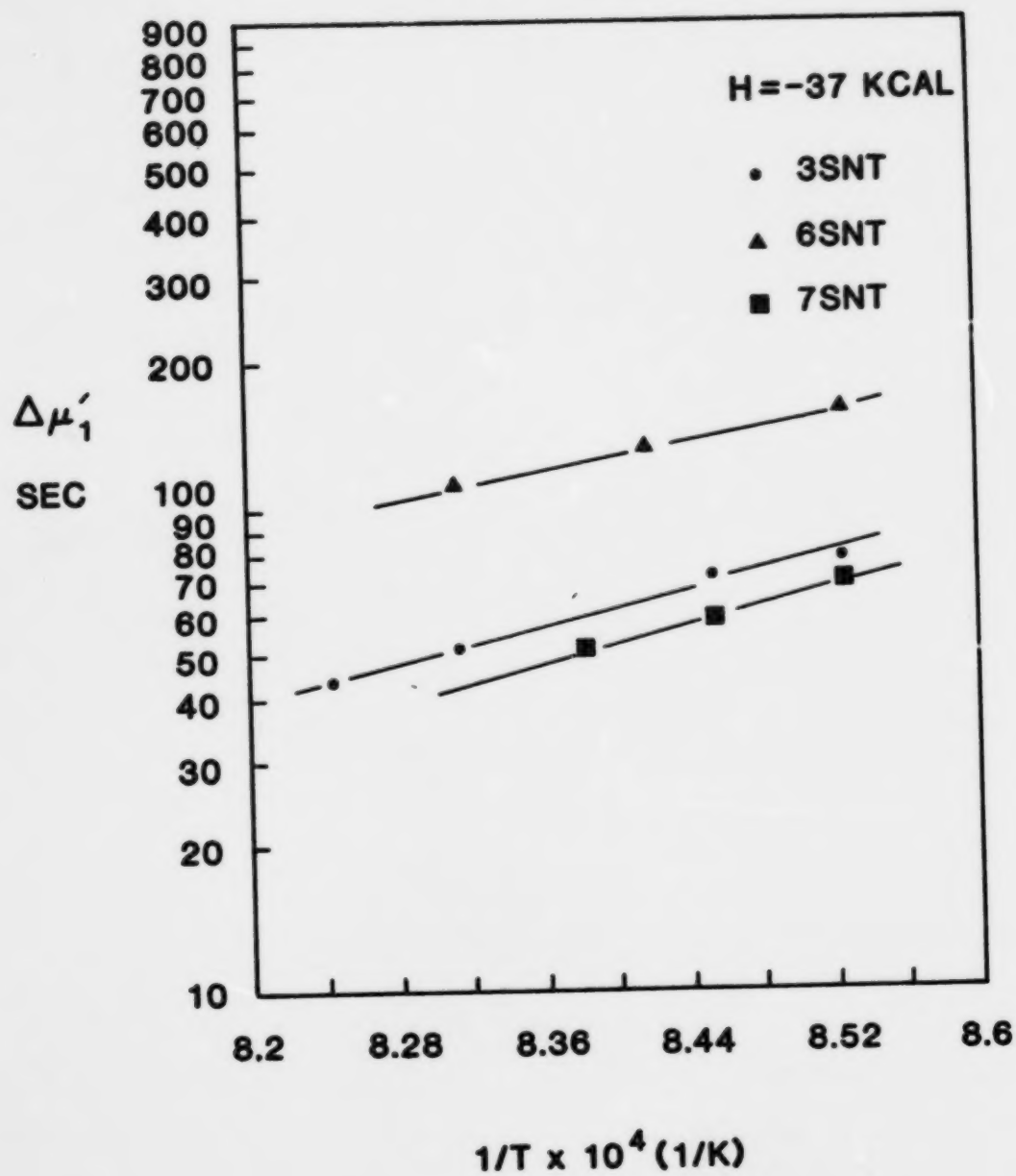


Figure 3.5 Temperature dependence of equilibrium absorption constant

relations between pore volume, diameter and grain size. The final stage results in pore coarsening and elimination over prolonged times (Kuczynski, 1976; Watanabe and Masuda, 1974).

A number of theoretical models have been proposed concerning the time dependence of surface area during intermediate stage sintering. One such model, the statistical model of Kuczinski (1976), describes this dependence as follows:

$$(S_i/S)^n - 1 = Bt = (1/S_r)^n - 1 \quad (3-21)$$

where S_i is the surface area at the onset of intermediate stage sintering and B is a parameter which depends on temperature and initial morphology. Figure 3.6 shows a plot of the pulsed derived values of $(1/S_r)^n - 1$, evaluated from equation 3-19 versus time for three sintering runs conducted at 930°C where $n = 2$. The plot results in reasonably straight lines for each of the runs; however, the parameter B appears to depend on $\Delta\mu_1^i(t_0)$, which is proportional to the initial surface area of the calcine immediately following decomposition. Figure 3.7 shows that B is roughly inversely proportional to $\Delta\mu_1^i(t_0)$.

This result suggests that the time dependence of the surface area of the calcine during sintering is described by the following form:

$$S_g^0((1/S_r)^2 - 1) = k(T) \cdot t \quad (3-22)$$

where S_g^0 is the initial specific surface area of the calcine following decomposition and $k(T)$ is a temperature-dependent sintering rate constant. By application of equations 3-17 and 3-18, equation 3-22 is rewritten in terms of the measured variable, $\Delta\mu_1^i(t_0)$, as shown:

$$(K_a(T^*)/K_a(T))\Delta\mu_1^i(t_0)((1/S_r)^2 - 1) = k^* \cdot t \quad (3-23)$$

where,

$$k^* = k(T) (L/V)K_a(T^*)\rho_c \quad (3-24)$$

and T^* is a convenient reference temperature which is taken to be 930°C in this case.

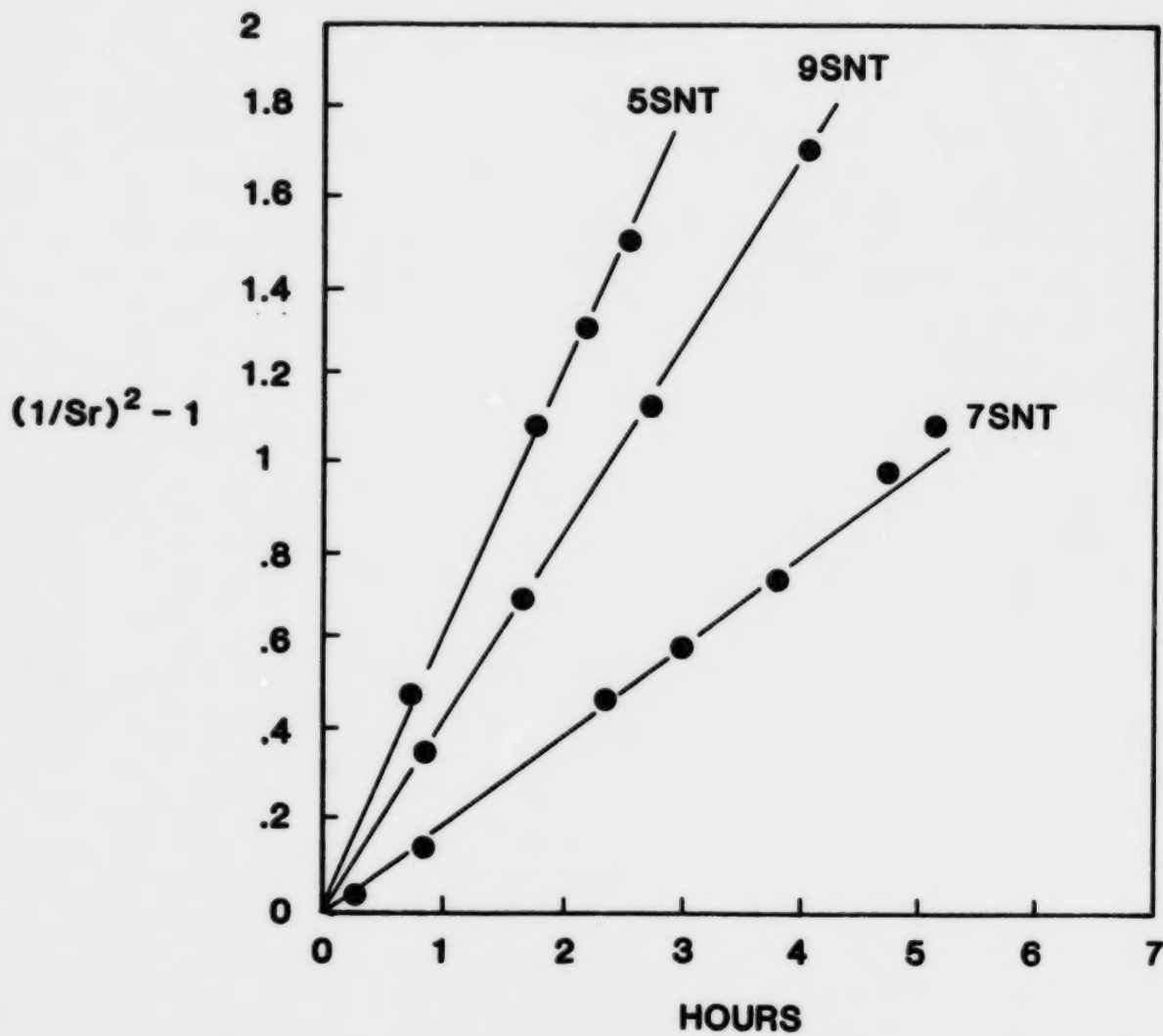


Figure 3.6 The linear dependence of $(1/Sr)^2 - 1$ on time, for different runs at 930°C

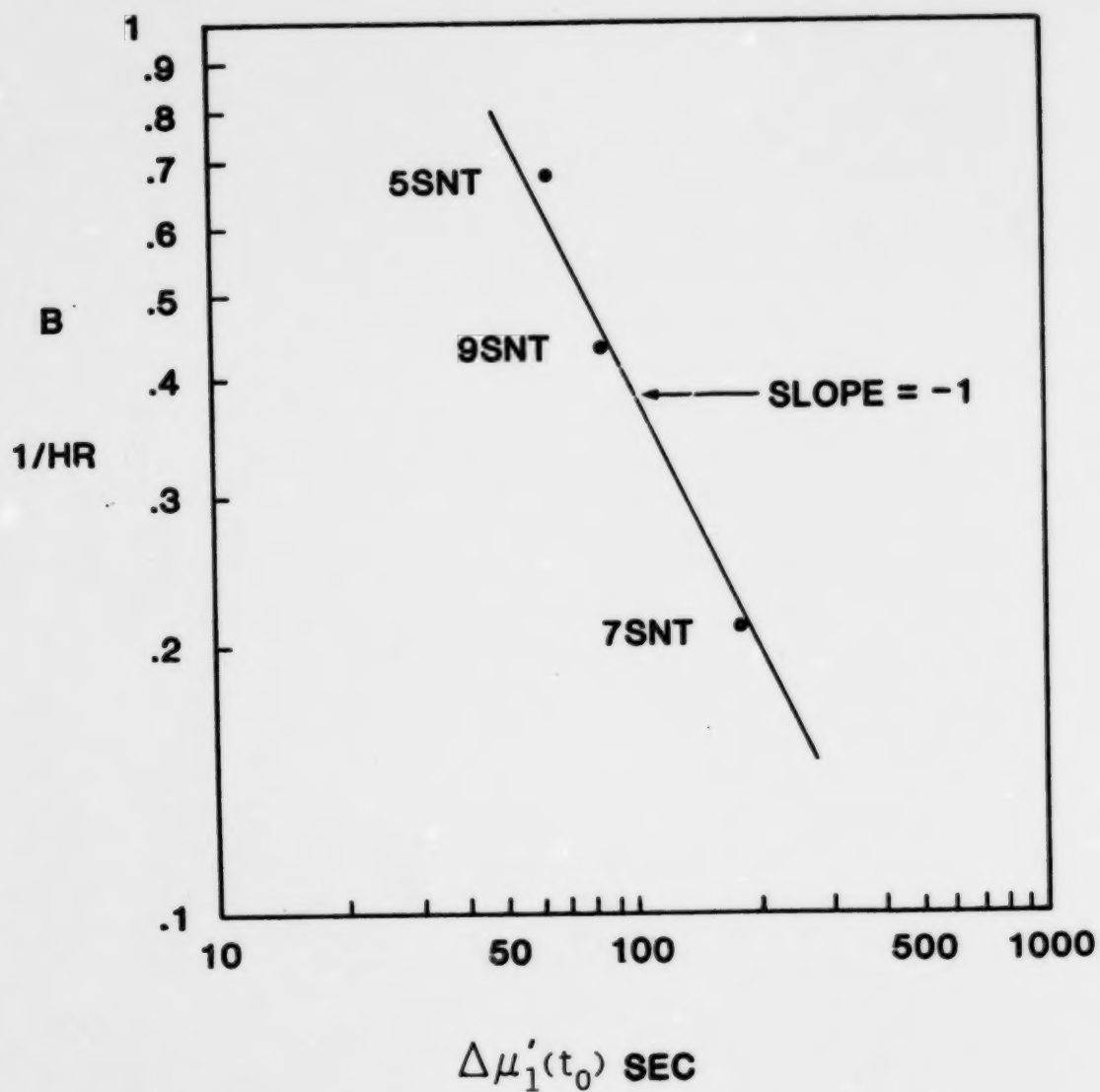


Figure 3.7 B vs $\Delta\mu_1'(t_0)$ for various sintering runs at 930°C

Figure 3.8 shows a plot of the left-hand side of equation 3-23 versus time for runs conducted at three different temperatures. k^* is evaluated from the slope of these curves. Figure 3.9 shows a plot of k^* versus $1/T$. The slope in Figure 3.9 results in a calculated value of activation energy for sintering of approximately 60 kcal/gmole. Using equation 3-24, the experimental results given an expression for k as follows:

$$k(T) = v \exp (-60,000/RT) \quad (3-25)$$

where, $v = 7.6 \times 10^{11} \text{ cm}^2/\text{g sec}$

3.8 DISCUSSION

The intermediate stage model of Kuczynski is derived primarily for the case of sintered powder compacts. In the development, it is assumed that a randomly distributed network of cylindrical pores pierce the sintered compact. Specific geometries concerning the grain and pore morphologies are assumed. Also, phenomenological relations between the porosity, grain and pore diameters (Zener relation) are applied.

The surface structure of the calcine precursor (Montana calcite) is shown by SEM in Figure 3.10. The surface texture of the calcite is observed to be smooth and continuous at both high and low magnification. Figure 3.11 shows the particle structure of a partially calcined sample. Low magnification reveals numerous fracture planes of approximately 20-40 μ in width. High magnification reveals the highly textured surface of the calcine. The surface appears to be composed of angular flakes with some discernible orientation of the flake planes.

The proposed assumptions contained in the Kuczynski model, and others of a similar nature, are likely to be at best only partially valid for the sintering of these structures. Consequently, the model described by equations 3-21 and 3-22 are considered to be correlations subject to meaningful physical interpretation only with the advent of improved theories concerning the sintering behavior of such morphologies. Differentiation of equation 3-22 results in an expression of the form:

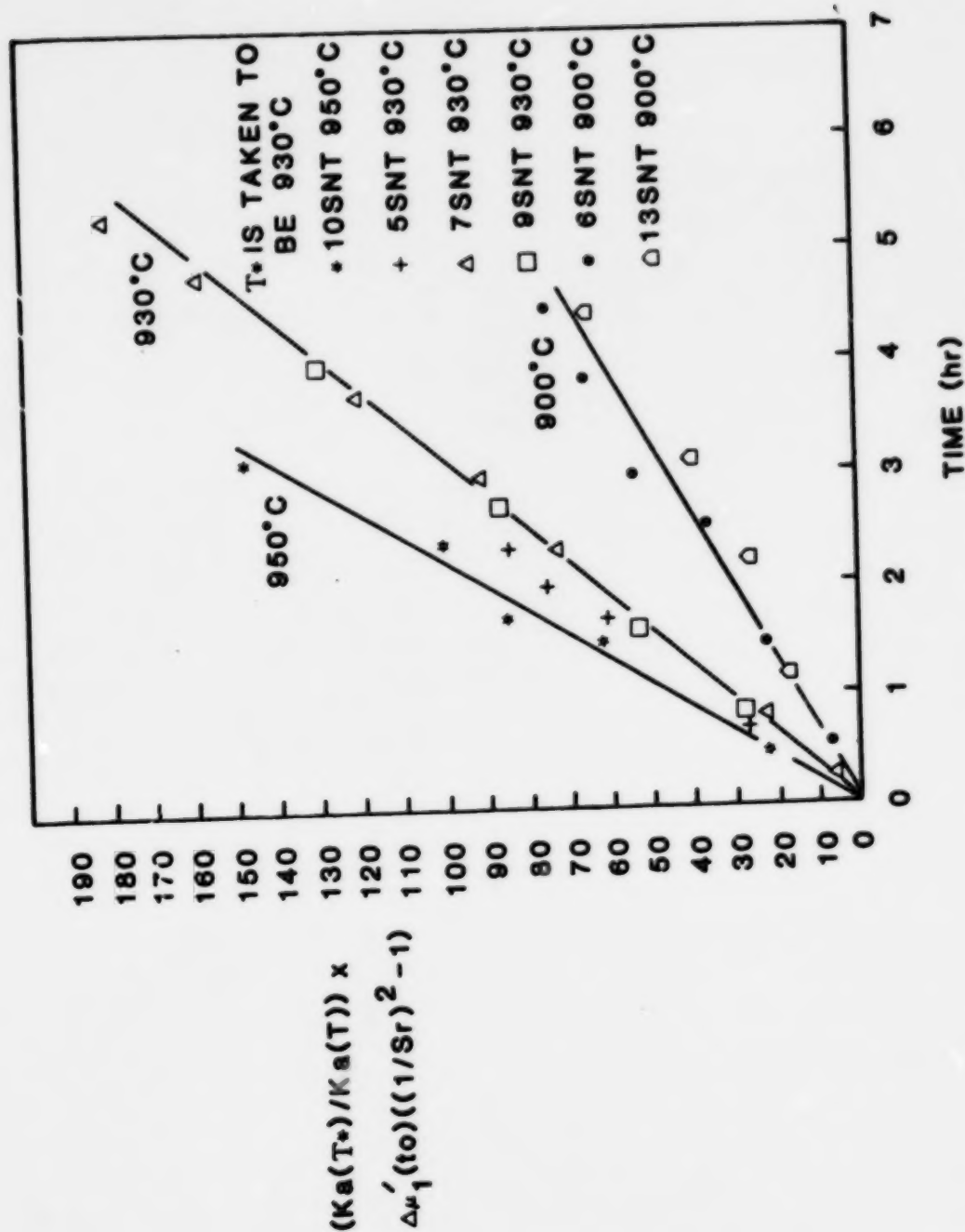


Figure 3.8 Surface area reduction vs. time for Montana calcite

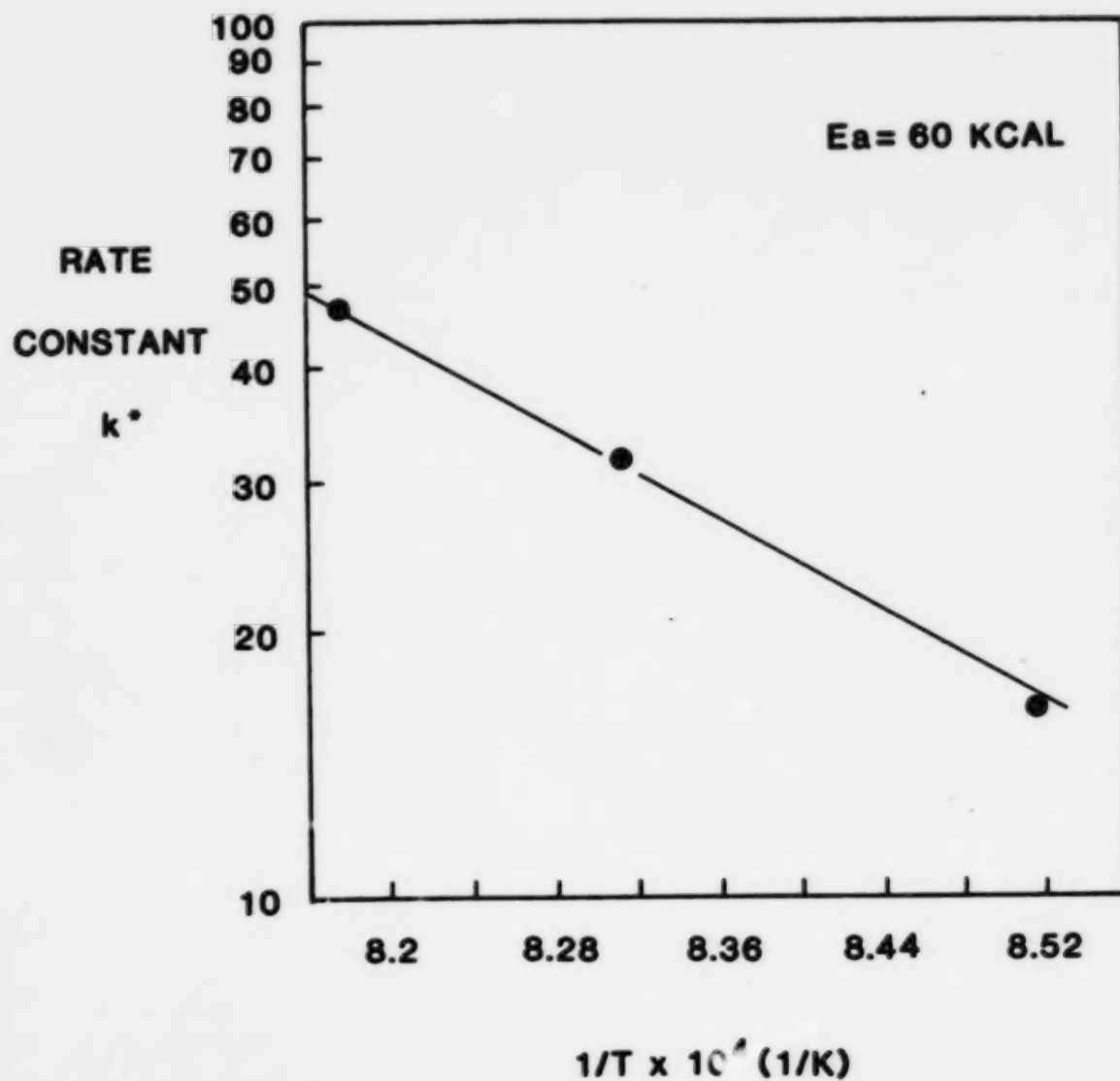


Figure 3.9 Temperature dependence of sintering rate constant

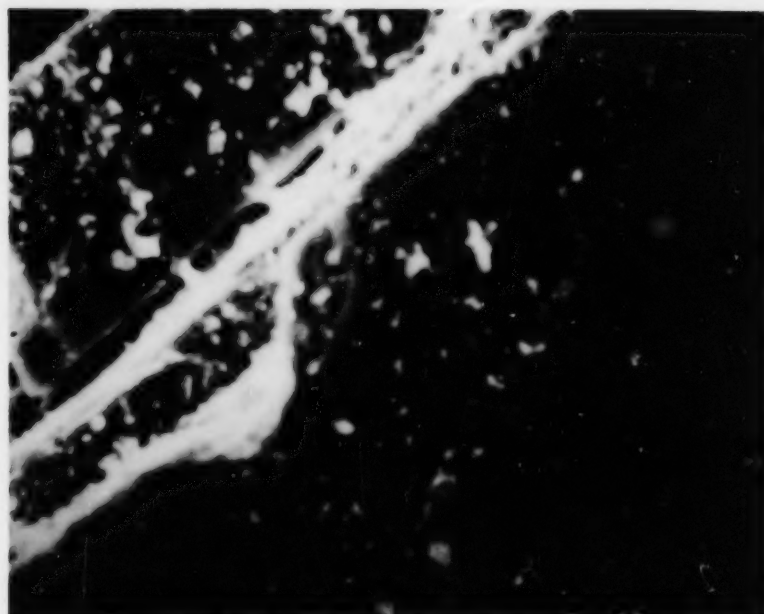
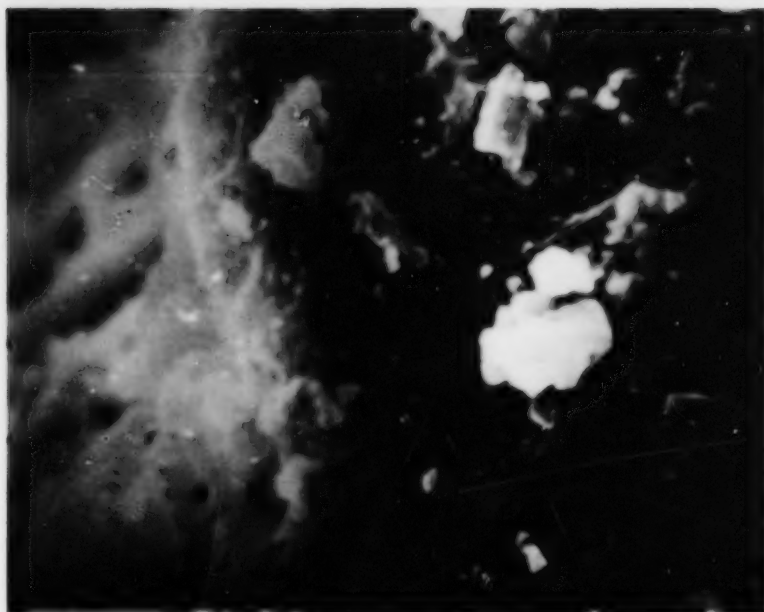


Figure 3.10 Typical surface texture of calcite

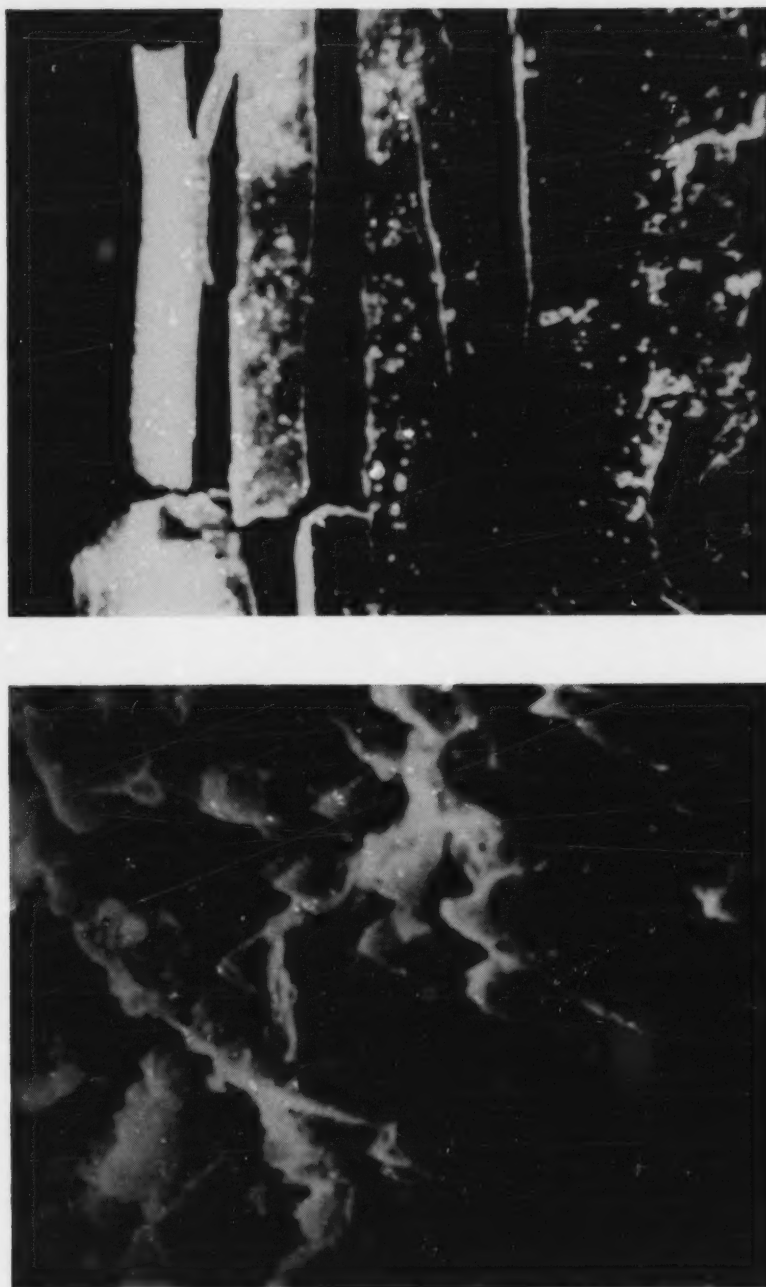


Figure 3.11 Typical surface texture of calcine

$$dS/dt = -k (S_g/S_g^0)^3 \quad (3-26)$$

This equivalent form reveals the unusual sintering behavior of these particular calcines compared to that of powder compacts formed from spherical grains. Equation 3-26 suggests that the absolute rate of change of surface area with respect to time is initially constant regardless of the initial value of surface area of the calcine. However, this rate of change diminishes less rapidly for calcines with a greater initial surface area. This peculiar result indicates that there may exist compensating effects concerning the sintering mechanism. The expected increased driving force for sintering of high surface area calcines appears to be offset by differences in the initial morphology of the calcine which results in reduced sintering rates. Offsetting influences may include such factors as grain size and shape, number of inter-granular contacts, porosity and pore size and shape distribution, and intra-granular strain.

If the kinetics parameters are substituted back into the model, one can predict the changes in the surface area. Figure 3.12 shows the rate of sintering at 1100°C for samples with different initial surface area. Figure 3.13 shows the effect of temperature on the surface area-time relation. Figure 3.14 shows the effect of the initial calcine surface area on the sintering relation.

The results of this study indicate that there exists a complex interaction between the rate of sintering and the specific solid structure of the virgin (unsintered) calcite calcine. In turn, the resulting solid morphology of the calcine appears to be particularly sensitive to decomposition conditions which include heating rate, calcination temperature and probably gas atmosphere.

3.9 CONCLUSIONS

A method has been described for monitoring changes in the surface area of calcines resulting from sintering using pulsed-gas chromatography. The results of this study indicate that surface area transformations

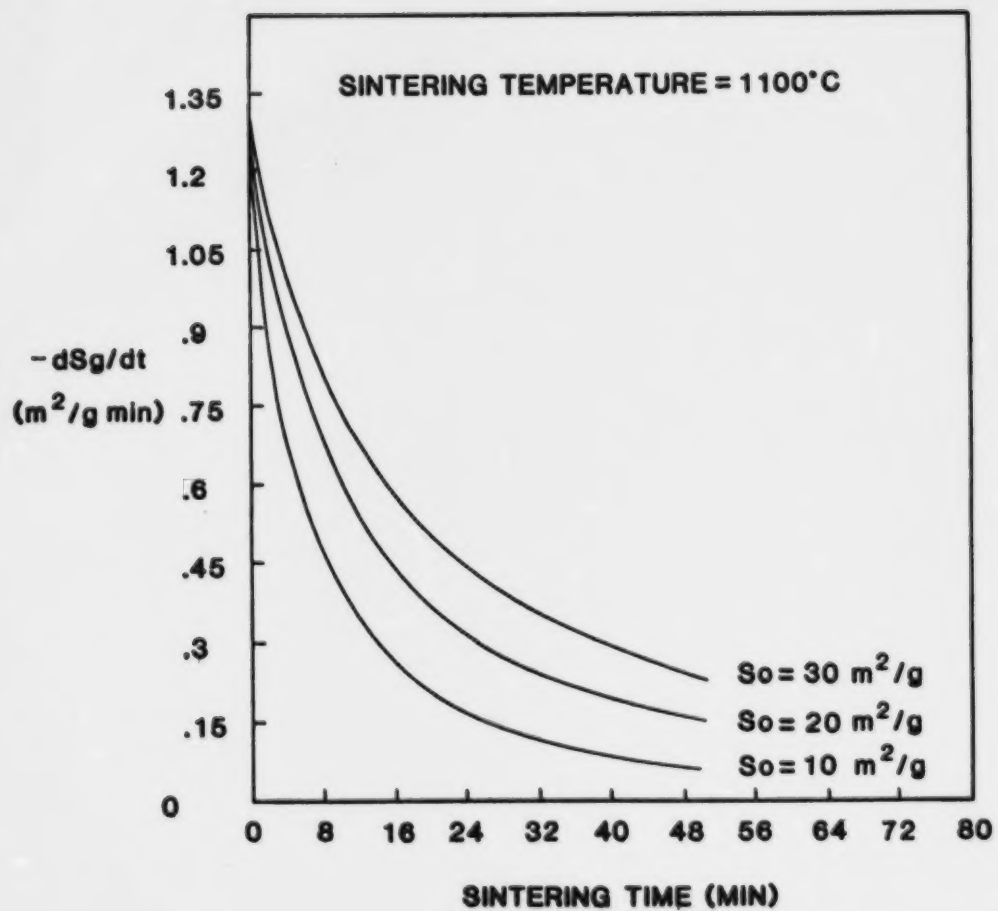


Figure 3.12 Simulated sintering at 1100°C: the effect of the initial surface area

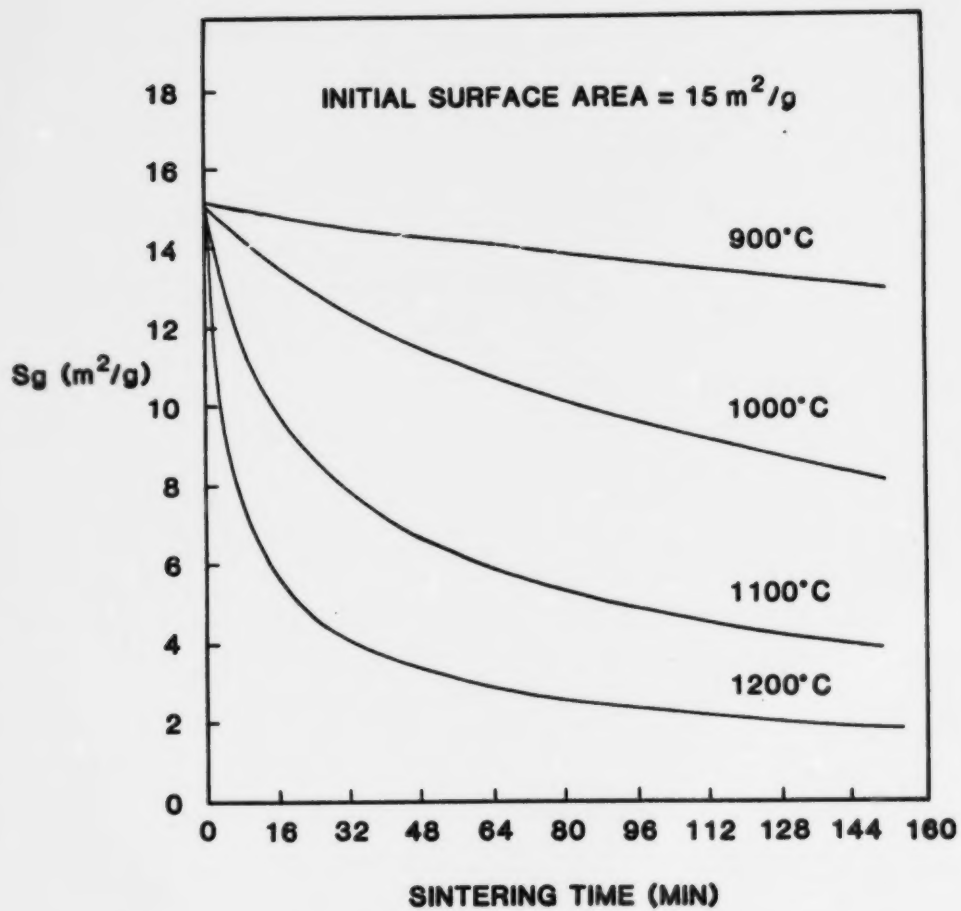


Figure 3.13 Simulated sintering: the effect of the sintering temperature

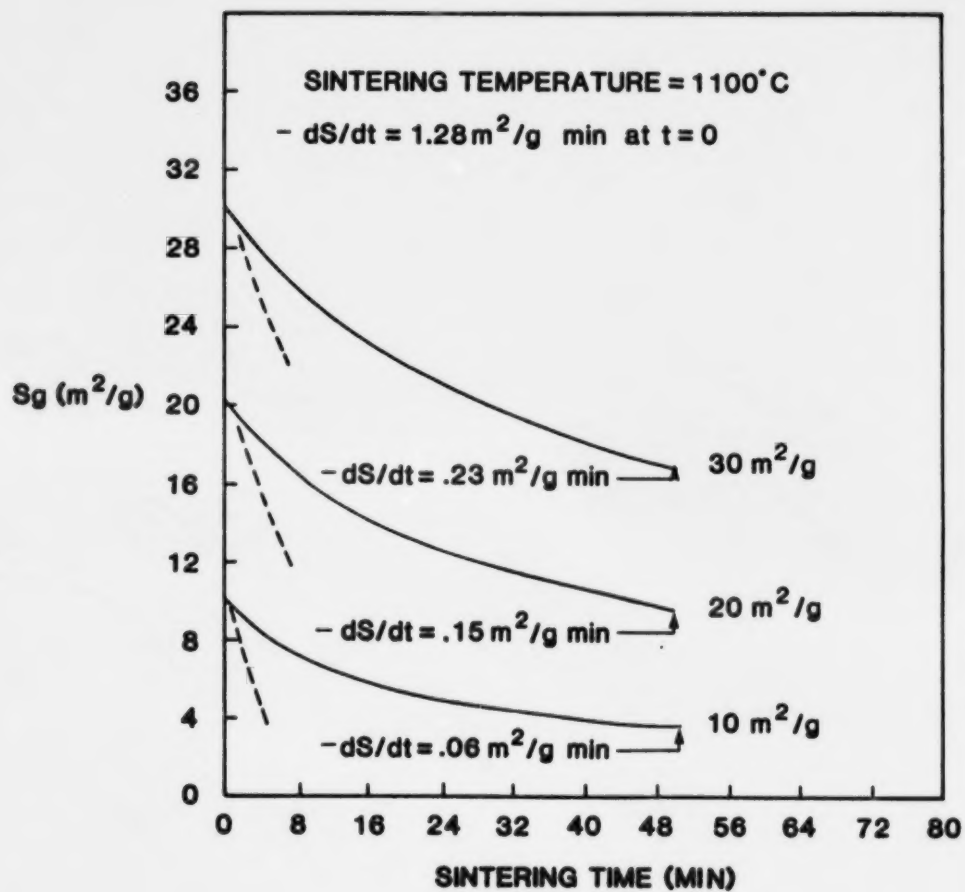


Figure 3.14 The dependence of the sintering-time relation on the initial surface area

can be successfully evaluated in situ and at high temperature using a combination of chemisorbing and nonadsorbing gas pairs.

Expressions derived in this study reveal the direct relation between specific surface area of the sample and the mean residence times for these gas pairs. These relations, which are shown to be valid for general classes of pellet geometries, pellet densification and radial structure nonuniformities, have been confirmed by comparison with BET surface measurements.

The time dependence of surface area during sintering of Montana calcite is correlatable by a form similar to the intermediate stage sintering model of Kuczynski. The rate of sintering appears to depend on the absolute value of surface area and on the initial calcite morphology. Based on the applied sintering model, the apparent activation energy for sintering is calculated to be 60 kcal/gmole.

The results of this study indicate that the use of pulsed-gas chromatography may be beneficially extended to high-temperature, in situ applications in order to evaluate pore structure transformations in reacting solids or catalysts at reaction conditions.

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3.11 APPENDIX

A model is described for characterizing the residence time distribution of an adsorbable tracer in a packed column containing porous pellets of arbitrary geometry. The local adsorption, transport and pore structure properties are assumed to vary through the radial coordinate of the pellet. The concentration, $C(z,t)$, of an adsorbable tracer as a function of time and axial column position is obtained by solution of the following material balance equations.

Model

The mass balance for tracer in the inter-pellet volume is given by:

$$\begin{aligned} (D_a/E) \partial^2 C / \partial z^2 - (V/E) \partial C / \partial z \\ - w(D_{e,N}(1-E)/RE)(\partial C_{i,N} / \partial r)_{r=R} = 0 \end{aligned} \quad (A-1)$$

w is a geometrical factor which equals three for spheres, two for semi-infinite cylinders, and one for semi-infinite slabs.

The pellet is assumed to have a multi-zoned structure as shown in Figure 3.1. The adsorption, transport and pore structure properties are constant within a single zone. The characteristic dimension of each zone may be taken as arbitrarily small as desired.

The mass balance for tracer in each zone, n , of the pellet is described by:

$$\begin{aligned} (D_{e,n}/B_n)(1/r^{w-1}) \partial / \partial r (r^{w-1} \partial C_{i,n} / \partial r) \\ - C_{i,n} / \partial t - (S_{v,n}/B_n) \partial C_{a,n} / \partial t = 0 \end{aligned} \quad (A-2)$$

where $S_{v,n}$ is the surface area per unit pellet volume of the n^{th} zone. Adsorption on the pore walls is assumed to be linear and of the form:

$$\partial C_{a,n} / \partial t = k_a(C_{i,n} - C_{a,n}/K_a) \quad (A-3)$$

The initial conditions are:

$$C = C_{i,n} = C_{a,n} = 0 \quad z > 0, t = 0 \quad (A-4)$$

The boundary conditions at the junction of each adjacent zone is given by:

$$C_n = C_{n+1} \quad r = r_n \quad (A-5)$$

$$D_{e,n} (\partial C_{i,n} / \partial r) = D_{e,n+1} (\partial C_{i,n+1} / \partial r)_{r=r_n} \quad (A-6)$$

for $n = 1, 2, \dots, N-1$

For zone one, the symmetry condition requires:

$$(\partial C_{i,1} / \partial r) = 0 \quad r = 0 \quad (A-7)$$

The external boundary condition for zone N is given as:

$$D_{e,N} (\partial C_{i,N} / \partial r)_{r=R} = k_f (C - (C_{i,N})_{r=R}) \quad (A-8)$$

The boundary conditions for the mobile (inter-pellet) phase are:

$$C = C_p(t) \quad z = 0 \quad (A-9)$$

and, $C(z,t)$ is bounded for all z .

Moment Characterization

The j^{th} unreduced absolute moment of the pulse residence time distribution is defined as:

$$\begin{aligned} \mu(j) &= \int_0^\infty t^j C(t) dt; \mu_{i,n}(j) = \int_0^\infty t^j C_{i,n}(t) dt \\ \mu_{a,n}(j) &= \int_0^\infty t^j C_{a,n}(t) dt \end{aligned} \quad (A-10)$$

and $\mu_p(j) = \int_0^\infty t^j C_p(t) dt$

Zeroth Moment

Equations (A-1) to (A-9) are transformed to zeroth moment expressions by integrating from zero to infinity. The following relations result.

$$\begin{aligned} (D_a/E) \partial^2 \mu(0)/\partial z^2 - (V/E) \partial \mu(0)/\partial z \\ - w(D_{e,N}(1-E)/RE)(\partial \mu_{1,N}(0)/\partial r)_{r=R} = 0 \end{aligned} \quad (A-11)$$

Intra-pellet phase:

$$(D_{e,n}/B_n)(1/r^{w-1}) \partial/\partial r (r^{w-1} \partial \mu_{1,n}(0)/\partial r) = 0 \quad (A-12)$$

Application of equation (A-12) and transformed boundary condition (A-7) results in:

$$\mu_{i,1}(0) = A_1 \quad \text{where } A_1 \text{ is a constant} \quad (A-13)$$

Successive solution for each zone applying the appropriate transformed boundary conditions results in the following relations:

$$\mu_{a,n}(0)/K_a = \mu_{i,n}(0) = \mu(0) \quad n = 1, 2 \dots N \quad (A-14)$$

and, of course, $\mu(0) = \mu_p(0)$.

From equation (A-14) it can be inferred that the zeroth moment of tracer concentration is constant everywhere within the pellet volume and equal to the zeroth moment in the mobile phase.

First Moment

Equations (A-1) to (A-9) are transformed to first moment expressions by multiplying by t and integrating from zero to infinity. The following relations for the transformed material balance equations result:

Inter-pellet Phase:

$$(D_{e,n}/B_n)(1/r^{w-1})(\partial/\partial r)(r^{w-1} \partial \mu_{i,n}(1)/\partial r) = -\Phi_n \quad (A-16)$$

where,

$$\Phi_n = (1 + S_{v,n} K_a/B_n) \mu_p(0) \quad (A-17)$$

From equation (A-16),

$$\partial \mu_{i,n}(1)/\partial r = - \beta_n \phi_n r / w D_{e,n} + B_n / r^{w-1} \quad (A-18)$$

where B_n is a constant. Successive application of the transformed boundary condition (A-8) results in the following general expression for B_n :

$$B_n = (1/w D_{e,n}) ((\beta_n \phi_n - \beta_{n-1} \phi_{n-1}) r_{n-1}^w \dots + (\beta_2 \phi_2 - \beta_1 \phi_1) r_1^w) \\ \text{for } n = 2, 3 \dots N \quad (A-19)$$

Substitution of equations (A-17) to (A-19) into (A-15) and solving results in the following expression for the absolute moment:

$$\mu_1^i = (L/V)(E + (1-E) \bar{B} + K_a(1-E) \bar{S}_v) + \mu_{1,p}^i \quad (A-20)$$

where,

$$\bar{B} = \sum_{n=1}^N \beta_n v_n \quad (A-21)$$

$$\bar{S}_v = \sum_{n=1}^N S_{v,n} v_n \quad (A-22)$$

$$v_n = (r_n^w - r_{n-1}^w) / R^w = \text{pellet volume fraction} \quad (A-23)$$

$$\text{and, } \mu_1^i = \mu(1)/\mu(0) \quad (A-24)$$

Thus, the first absolute moment of the pulse depends only on the volume averaged local porosity and local surface area per unit pellet volume. The first absolute moment shows no dependence on the specific distribution of these local properties in the radial dimension of the pellet.

3.12 NOTATION

- A = Constant defined in eq. 3-18
 B_n = Constant defined in eq. A-19
 C = Concentration of tracer in mobile phase; mole/cc
 $C_{i,n}$ = Concentration of tracer in intra-pellet pore volume; mole/cc
 $C_{a,n}$ = Adsorbate concentration on pore walls; moles/cm² surface
 D_a = Effective axial dispersion coefficient; cm²/sec
 $D_{e,n}$ = Effective intra-pellet diffusivity; cm²/sec
 E = Bed voidage; cc column void/cc column volume
 K_a = Equilibrium adsorption constant defined in eq. 3-4; (mole/cm²)/(mole/cc)
 k_a = Adsorption rate constant; cm/sec
 k_f = Particle to gas mass transfer coefficient; cm/sec
 k = Sintering rate constant defined in eq. 3-22; cm²/g-sec
 k^* = Dimensionless sintering rate constant defined by eq. 3-24
 L = Packed column length; cm
 r = Pellet coordinate; cm
 r_n = Intra-pellet coordinate of junction between zone n and $n+1$; cm
 R = Pellet radius; cm
 S_g = Specific surface area; cm²/g
 S_g^0 = Specific surface area immediately following complete calcination; cm²/g
 S_r = Relative surface area defined in eq. 3-19
 $S_{v,n}$ = Surface area per unit volume of pellet in n^{th} zone; cm⁻¹
 $\bar{S}_v$ = Volume averaged surface area per unit pellet volume (see eq. 3-14; cm⁻¹

- t = Sintering time as measured relative to reference time; sec
 t_o = Reference time taken as the point of complete calcination; sec
 T = Sintering temperature; °C
 T^* = Reference temperature taken here as 930°C
 V = Superficial velocity of helium carrier; cm/sec
 v_n = Volume fraction in n^{th} zone given by eq. 3-15
 w = Geometric factor for sphere, semi-infinite cylinder and slab
 z = Axial column coordinate; cm

3.13 GREEK LETTERS

- β_n = Porosity of n^{th} zone
 $\bar{\beta}$ = Volume averaged pellet porosity defined by eq. 3-13
 μ_1^i = First absolute moment of tracer concentration in mobile phase defined in eq. 3-11; sec
 $\Delta\mu_1^i$ = Time lag of mean residence time of an adsorbable tracer relative to a nonadsorbable tracer defined in eq. 3-16; sec
 $\mu_{1,non}^i$ = Mean residence time of a nonadsorbable tracer at sintering time t ; sec
 $\mu(j)$ = j^{th} unreduced absolute moment of tracer in mobile phase, defined in eq. (A-10); (mole/cc) sec^{j+1}
 $\mu_{i,n}(j)$ = j^{th} unreduced absolute moment of tracer in zone n of the intra-pellet volume, defined in eq. (A-10); (mole/cc) sec^{j+1}
 $\mu_{a,n}(j)$ = j^{th} unreduced absolute moment of adsorbate in zone n , defined in eq. (A-10); (mole/cm²) sec^{j+1}
 $\mu_p(j)$ = j^{th} unreduced absolute moment of tracer at inlet to column, defined in eq. (A-10); (mole/cc) sec^{j+1}
 ρ_c = Apparent column density; g-solid/cc column volume
 ϕ_n = Defined in eq. (A-17)

CHAPTER 4
APPLICATION OF PULSED-GAS CHROMATOGRAPHY TO
MONITOR STRUCTURAL AND TRANSPORT PROPERTY
TRANSFORMATIONS IN A REACTING SO_2 -LIME SYSTEM

4.1 INTRODUCTION

The transformations of the solid structure of lime and its effect on the porosity and mass transport properties of gases in it as it reacts with sulfur dioxide, SO_2 , and air were investigated using pulsed-gas chromatography. The carrier media utilized was helium and the temperature range was 850-1000°C. Following calcination, the lime particles are exposed to a flowing mixture of SO_2 and air. At various time intervals, pulses of argon tracer are injected into the column. The dispersion of the tracer pulse at each sample point is characterized by moment analysis. The time series of pulses, which are collected over the full range of attainable conversions, provides a semi-quantitative measure of the conversion-time behavior and the effect of conversion on the intra-particle mass transport properties of the solid.

The results of this investigation indicate that the pulsed chromatographic method is adaptable to in situ, high-temperature measurement. The method is shown to provide a qualitative insight into the effect of sulfation conditions on the mass transport and conversion behavior of the SO_2 -lime system. The pulse derived data are consistent with the observations of Borgwardt and Harvey (1972) and Hartman and Coughlin (1976) which indicate that increased temperature and SO_2 concentration results in enhanced initial reaction rates but diminished limiting conversions. The critical behavior of the intra-particle mass transport properties near the limiting conversion is clearly identified from pulse analysis. The results reveal that for a given level of average particle conversion, process conditions which tend to accelerate the rate of reaction also give rise to increased mass transfer resistances. The

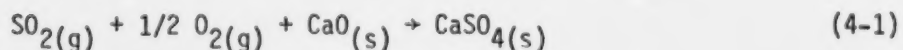
pulse-derived data are successfully interpreted in terms of a pore plugging model such as those described in previous publications (Hartman and Coughlin, 1976; Bhatia and Perlmutter, 1981).

Low to moderate temperature pulsed-gas chromatography has previously been employed to measure adsorption and transport parameters in porous solids (Ma and Mancel, 1972; Scott et al., 1974; Chihara et al., 1978). The primary interest in these studies was to derive process-oriented data. A few studies have been conducted for the purpose of evaluating the effect of solid structure transformations (gasification, fouling) on transport parameters (Butt et al., 1975; Debelak et al., 1982; Attar and Warren, 1983). Each of these studies was conducted at relatively low temperatures and required removal of the porous solid from the reaction chamber or conditions.

The purpose of this investigation is to explore the relations between solid conversion and the transport and structure properties of a reacting system using in situ, high-temperature pulsed-gas chromatography. A primary goal of this study is to establish if the method has sufficient sensitivity to detect changes in transport and structure variables over any range of solid conversion. It is also the purpose of this investigation to evaluate the effect of reaction conditions on the conversion relations and to determine if the trends observed from the pulse-derived data are consistent with presently accepted fluid-solid reaction models. The experimental work reported here specifically addresses the reaction between SO_2 and lime which has practical implications for removal of sulfur-containing species from flue gas streams of coal-fired boilers.

4.2 SO_2 -LIME REACTION

The stoichiometry of the SO_2 -lime reaction is shown below.



Typically, the CaO reactant is formed from calcination of a parent

carbonate which results in a highly porous solid. Assuming negligible initial porosity for the carbonate and no particle shrinkage during the calcination reactions, the theoretical porosity of the lime before sulfation is approximately 0.69.

Since the molar volume of the sulfate is larger than that of the parent carbonate, the maximum attainable conversion for reaction (4-1) is limited. This limit is calculated by considering the extent of reaction when all of the pore volume is filled with product. The maximum theoretical conversion is calculated as follows:

$$x_{\max} = \frac{\beta_0}{(Z-1)(1-\beta_0)} \quad (4-2)$$

For pure lime, Z is the ratio of product to reactant molar volumes and has a value of 3.09 and β_0 is the initial lime porosity with value 0.517. Calculations show $x_{\max}$ to be about 0.69.

The experimental findings of Borgwardt and Harvey (1972) and Hartman and Coughlin (1976) indicate that for large particles the practical conversion limits are often well below those predicted by equation (4-2). The results of these studies also show that as the temperature and the SO_2 concentration are increased, the initial rate of reaction increases, but the limiting conversion is diminished. Borgwardt suggests that for reaction at 980°C the effectiveness factor approaches one only for particles smaller than $100\ \mu$. Borgwardt also shows that the effectiveness factor for reaction is closely related to the pore structure of the calcine, with smaller mean radius pores yielding lower effectiveness factors.

It is evident from these studies that the evolving mass transport properties of the solid reactant significantly affects both the instantaneous reaction rate and the maximum practical conversion limit. A number of investigators have incorporated the effects of reaction rate, intra-particle mass transport, product layer diffusivity and changing pore structure into models that seek to account for the conversion behavior of the solid reactant (Hartman and Coughlin, 1976; Ramachandran and Smith, 1977; Christowski and Georgakis, 1978; Bhatia and Perlmutter, 1981a, 1981b).

A number of these models can be described by the following general dimensionless form (for example, see Bhatia and Perlmutter, 1981a, 1981b):

$$\frac{1}{n^2} \frac{\partial}{\partial n^2} D_e n^2 \frac{\partial C}{\partial n} = \varphi^2 \frac{d}{d\tau} \quad (4-3)$$

$$\frac{dx(n)}{d\tau} = f(x(n), C(n), Bi, \psi_i) \quad (4-4)$$

$$D_e(n) = g(n) \quad (4-5)$$

$$\bar{x} = 3 \int x(n) n^2 dn \quad (4-6)$$

An important consequence of these models is that for a given initial calcine, the local conversion, $x(n)$, and the average pellet conversion, $\bar{x}$, are completely determined as a function of a single time constant once values for the Thiele modulus, φ , and modified Biot modulus, Bi , are specified. From a purely mathematical perspective, the only difference between the various models is in the explicit descriptions of functions f and g in equations (4-4) and (4-5). For our purposes, the most important conclusions concerning the particular solutions of these models are the common predictions which are summarized here:

- A. Process conditions which tend to increase the reaction rate through an increase in either the chemical rate constant, k_s , the product layer diffusivity, D_s , or the gas reactant concentration will generally result in diminished limiting conversions due to accelerated pore mouth plugging (strictly valid when $x_{\max} \rightarrow 1$).
- B. For a given level of average pellet conversion, process conditions which increase the initial reaction rate will be reflected in diminished mass transfer rates for some range of conversion. This condition is likely to become most evident when the average pellet conversion is such that the local porosity near the pellet surface approaches zero.

It is perhaps instructive to gauge the qualitative validity of the pulse technique in terms of its ability to identify the general conditions mentioned above.

4.3 PULSED-GAS CHROMATOGRAPHY

The pulsed-gas chromatographic technique is useful in obtaining parametric values relevant to the interaction of a tracer with a porous solid. The method that has been described in previous publications (Schneider and Smith, 1968; Hsu and Haynes, 1981) involves the injection of a tracer pulse into a column packed with a porous solid. The tracer pulse is carried through the column by a flowing medium. A detector monitors the residence time distribution of the tracer as it exits the column. Values of the interaction parameters are reflected in the specific features of the effluent wave. Fourier (Gangawal et al., 1971) and moment analysis is the most common method for characterizing features of the tracer residence time distribution and for fitting model parameters.

In order to apply the method, a model is formulated which describes the residence time distribution as a function of the model parameters. A chromatographic model has been presented in a number of publications (Kucera, 1965; Kubin, 1965; Schneider and Smith, 1968) and will not be repeated here. The solution of this model in terms of moments of the pulse distribution for a nonadsorbable tracer is given by:

$$\mu_1' = \frac{L}{V} \left(1 + \frac{(1-E)}{E} \beta \right) \quad (4-7)$$

$$\mu_2' = \frac{2L}{V} \left[\frac{D_a}{EV^2} \left(1 + \frac{(1-E)}{E} \beta \right)^2 + \frac{R^2}{15} \frac{(1-E)}{E} \beta^2 \left(\frac{1}{D_i} + \frac{5}{k_f R} \right) \right] \quad (4-8)$$

where,

$$\mu_1' = \int_0^\infty t C(L,t) dt / \int_0^\infty C(L,t) dt \quad (4-9)$$

$$\mu_2' = \int_0^\infty (t - \mu_1')^2 C(L,t) dt / \int_0^\infty C(L,t) dt \quad (4-10)$$

and V is the average interstitial velocity of the carrier gas, D_a is the effective axial dispersion coefficient, D_i is the effective intraparticle diffusivity, k_f is the gas-to-particle mass transfer coefficient and β is the particle porosity. For most cases, $k_f R \gg D_i$; thus the third term in equation (4-8) can generally be ignored.

The derivation of equations (4-7) and (4-8) assumes that the local particle porosity and local intra-particle diffusivity is constant throughout the particle radius. The presence of intra-particle concentration gradients during the sulfation of lime will result in the development of particles with radially nonhomogeneous properties. Warren and Attar (1983) have shown that equation (4-7) is strictly valid for $\bar{\beta}$ interpreted as the average particle porosity, $\bar{\beta}$, regardless of the radial distribution. It is a relatively simple matter to show that $\bar{\beta}$ may be rigorously substituted for β in the axial dispersion term of equation (4-8). The intra-particle dispersion term, however, becomes a complicated function of the local porosities and diffusivities of the particle. We may replace β^2/D_i in the second term of equation (4-8) by $\bar{\beta}^2/D_i^*$ recognizing that D_i^* represents some averaged measure of the resistance to mass transport inside the pellet. Equations (4-7) and (4-8) are rewritten in terms of the substitutions mentioned above.

$$\mu_1 = \frac{L}{V} \left(1 + \frac{(1-E)}{E} \bar{\beta} \right) \quad (4-10)$$

$$\mu_2' = \frac{2L}{V} \left[\frac{D_a}{EV^2} \left(1 + \frac{(1-E)}{E} \bar{\beta} \right)^2 + \frac{R^2}{15} \frac{(1-E)}{E} \frac{\bar{\beta}^2}{D_i^*} \right] \quad (4-11)$$

Because of the practical high-temperature limitations of the injector and detector systems, a carrier gas pre-heat and post-cooling column is required in addition to the fixed-bed column. Account must be made of the dispersion and residence time effects in these extra column spaces. Providing that the dispersion processes in these sections are linear, equations (4-11) and (4-12) may be modified to include these effects by addition of a simple constant. The additive nature of the mean residence time and pulse variance for the case of axial dispersion alone is discussed by Levenspiel and Bischoff (1963).

The resulting expressions for the first and second moments are given as:

$$\mu_1^* = \mu_{1,ext}' + \mu_1' \quad (4-12)$$

$$\mu_2^* = \mu_{2,ext}' + \mu_2' \quad (4-13)$$

where $\mu_{1,\text{ext}}^*$ and $\mu_{2,\text{ext}}^*$ account for the extra column effects and are constants for a given set of process conditions.

In order to monitor the effect of reaction on solid structure, we may look upon the quantity, $\Delta\mu_1^*$, which is defined as:

$$\Delta\mu_1^*(t_s) = \mu_1^*(t_s) - \mu_1^*(0) = A_1 \Delta\bar{\beta}(t_s) \quad (4-14)$$

where,

$$\Delta\bar{\beta}(t_s) = \bar{\beta}(t_s) - \bar{\beta}_0 \quad (4-15)$$

$$\text{and, } A_1 = \left(\frac{L}{V}\right)(1-E)/E \quad (4-16)$$

t_s refers to the sulfation time, $\mu_1^*(0)$ is the mean residence time for a tracer pulse over the unsulfated calcine and β_0 is the initial calcine porosity. Assuming that the particle radius is unchanged during sulfation, it directly follows that E , V , D_a and therefore A_1 are independent of solid conversion. The change in solid porosity as a result of reaction is then easily calculated from measured pulse response as shown:

$$\Delta\bar{\beta}(t_s) = \Delta\mu_1^*(t_s)/A_1 \quad (4-17)$$

Assuming that the porous network remains well connected, the average extent of reaction, $\bar{x}$, is described by the following relation:

$$\bar{x}(t_s) = \frac{(\beta_0 - \bar{\beta}(t_s))}{(Z-1)(1-\beta_0)} = \frac{-\Delta\mu_1^*(t_s)/A_1}{(Z-1)(1-\beta_0)} \quad (4-18)$$

The above relations show that both the extent of reaction and the average pellet porosity are simply related to the pulse response quantity, $\Delta\mu_1^*(t_s)$. It can be seen that a time series of pulses provides complete information relevant to the conversion-time history of the particle.

From equations (4-12) and (4-13) it is easily shown that $\Delta\mu_2^*(t_s)$ is given by the following form:

$$\begin{aligned}\Delta\hat{\mu}_2^* &= \alpha_1 + \alpha_2 \bar{\beta}(t_s) + \alpha_3 \bar{\beta}^2(t_s) + \alpha_4 (\bar{\beta}^2(t_s)/D_i^* - \bar{\beta}_0^2/D_i^*(0)) \\ &= \varphi_{AX} + \varphi_i\end{aligned}\quad (4-19)$$

where α_1 is a simple constant with magnitude less than zero and is given by:

$$\alpha_1 = \frac{-2L}{V} \left(\frac{D_a}{EV^2}\right) \left(\frac{1-E}{E}\right) (2\beta_0 + \frac{(1-E)}{E} \beta_0^2) \quad (4-20)$$

α_2 , α_3 and α_4 are simple constants with magnitude greater than zero. Expressions for these constants are:

$$\alpha_2 = \frac{4L}{V} \left(\frac{D_a}{EV^2}\right) \left(\frac{1-E}{E}\right) \quad (4-21)$$

$$\alpha_3 = \frac{2L}{V} \left(\frac{D_a}{EV^2}\right) \left(\frac{1-E}{E}\right)^2 \quad (4-22)$$

$$\alpha_4 = \frac{2LR^2}{15V} \frac{(1-E)}{E} \quad (4-23)$$

and φ_{AX} and φ_i are terms representative of the contribution to the change in pulse variance due to axial dispersion and intra-particle mass transport and are given by:

$$\varphi_{AX} = \alpha_1 + \alpha_2 \bar{\beta} + \alpha_3 \bar{\beta}^2 \quad (4-24)$$

$$\varphi_i = \alpha_4 [\bar{\beta}^2/D_i^* - \beta_0^2/D_i^*(0)] \quad (4-25)$$

It is evident that for constant D_i^* , $\Delta\mu_2(t_s)$ decreases monotonically for decreasing values of $\bar{\beta}(t_s)$, or equivalently for increasing values of $-\Delta\mu_1^*(t_s)$. Consequently, a positive slope for the curve $\Delta\mu_2^*(t_s)$ versus $-\Delta\mu_1^*(t_s)$ provides a necessary and sufficient condition for inferring that the intrapellet mass transport resistances are increasing (D_i^* is decreasing) with progressive solid conversion. Based on the random pore model of Wakao and Smith (1962), the local intra-particle diffusivity is expected to depend on local porosity in the following manner:

$$D_i = \beta^2 D_K \alpha^2 \propto \beta^{5/2} \quad (4-26)$$

where it is assumed that diffusion is in the Knudson regime. The dependence of D_i on β suggests that the intra-particle dispersion term, φ_i , in equation (4-26) is continuously increasing with conversion. Though φ_i may increase continuously with $\bar{x}$, the slope of $\Delta\mu_2^*$ versus $\bar{x}$ will become positive only when $(d\varphi_i/d\bar{x}) > |(d\varphi_{AX}/d\bar{x})|$. The behavior of $\Delta\mu_2^*$ versus $\bar{x}$ is shown schematically in Figure 4.1.

A rapidly increasing slope for a plot such as that in Figure 4.1 is indicative of a critical point in the relation between the mass transport characteristics of a solid and the conversion variable. Such behavior is expected to occur near the point of pore mouth plugging where diffusion into the particle becomes limited by the small pore dimensions and the mechanism of diffusion becomes an activated process.

4.4 EXPERIMENTAL

A schematic of the experimental apparatus is shown in Figure 4.2. During the pulse analysis phase, helium carrier gas is directed into the column through an 8-port injector valve, IV. The column and preheat coil are contained in a rheostat-controlled, high-temperature furnace. The column is a 25 cm long, 1/4" standard O.D. stainless steel tube. The column is initially charged with 12/20 mesh Montana calcite, a relatively pure and highly crystalline carbonate. Upon exiting the column, the carrier gas is directed into a thermal conductivity detector, TCD. An analog to digital converter, AD1, digitizes the detector signal under computer control, CP1 (Dec System; Minc 11). The argon tracer, which is purged through a 50 L sample loop at IV, is injected into the carrier stream by manual manipulation of the sample valve. The tracer pulse is characterized by a minimum of 100 sample points. Integration of the pulse data is performed to calculate moments of the pulse distribution. Typically, three or four pulses are taken for each time point. The reproducibility of the first absolute and second central moments is generally in the range of ± 0.07 sec and ± 0.10 sec, respectively.

During the sulfation phase, the helium carrier gas bypasses the column through valve BV1. The flow of SO_2 and air are monitored through

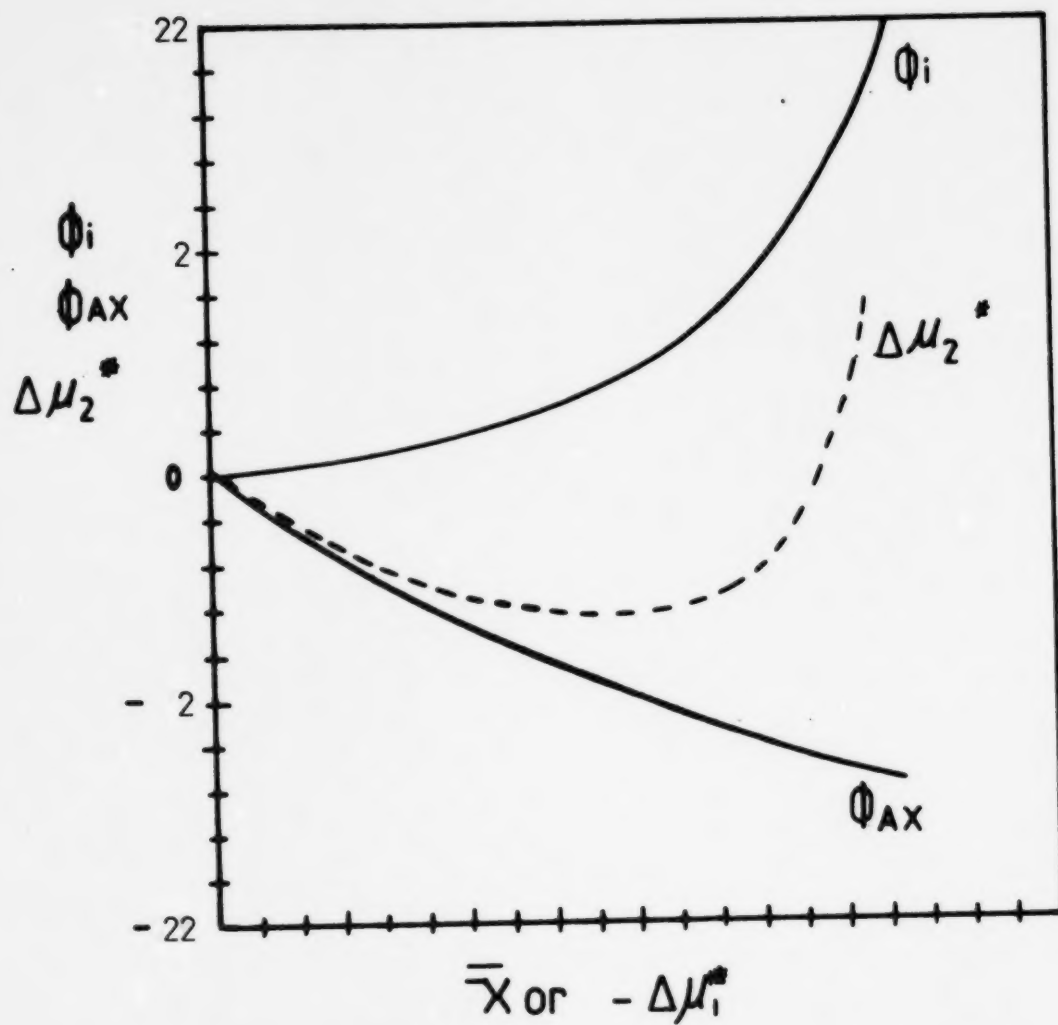


Figure 4.1 The effect of conversion on pulse dispersion: contribution of axial and intra-particle dispersion terms

[illegible]

Figure 4.2 Flow scheme and configuration options for pulse apparatus

flow meters F1 and F2. The volume percent of SO_2 in the reaction mixture is varied from 3-6% for various runs. The average interstitial velocity of the reaction mixture in the column is approximately 350 cm/sec. Following sulfation, the column is purged with air for a period of 5 minutes.

An experimental run is initiated by heating the high-temperature furnace to 900°C and holding for approximately two hours until complete calcination of the virgin calcite charge. Following calcination, the furnace is stabilized at the desired sulfation temperature. Prior to sulfation, an initial tracer pulse is injected and recorded. Runs at three temperatures ranging from 850°C to 950°C were performed. By alternating between discrete sulfation and pulse analysis phases, a time series of pulse data is generated over a wide range of solid conversion.

The practical limitations of the pulse chromatographic method require that a sufficiently large quantity of solid be contained in the column reactor in order to obtain the necessary sensitivity to measure the effect of changing solid structure on pulse dispersion. For the SO_2 -lime reaction, this requirement limits the potential for operating the in situ reaction in a differential mode. Initially, the solid conversion will occur progressively down the column length. Therefore, the pulse data contains information relevant to the average column characteristics. Despite this limitation, it is believed that the general trends observed concerning the relation between process conditions, conversion-time behavior and intra-particle mass transport characteristics are at least qualitatively valid.

4.5 RESULTS

It has been experimentally observed (Borgwardt and Harvey, 1972) that the resulting porosity in typical calcines is well predicted by the assumption of little or no particle shrinkage. Therefore, it is assumed in the following calculations that the initial calcine porosity is approximately .5. The maximum theoretical conversion is calculated from equation (4-2) to be .48. For all runs, the bed voidage and mean

interstitial carrier velocity is nearly constant and equal to .47 and 7.5 cm/sec. Introducing these quantities into equation (4-15) yields a value of $-\Delta\mu_{1,\max}^{\dagger}$ equal to 1.88, which corresponds to complete utilization of the initial calcine pore space.

Figure 4.3 shows a plot of $-\Delta\mu_1^{\dagger}$ versus sulfation time for three different sulfation temperatures. $-\Delta\mu_{1,\max}^{\dagger}$ ($\bar{x} = .48$) is indicated in the figure by the upper dashed line. It is evident that the limiting conversion for all runs is well below the theoretical maximum. As the sulfation temperature is increased from 850°C to 950°C, the value of the limiting conversion drops from 79% of the theoretical limit to only 48%.

By application of a random pore model to the data of Borgwardt and Harvey (1972), Bhatia and Perlmutter (1981) calculate the activation energy for the chemical reaction rate constant and the product layer diffusivity to be 56.4 MJ/kmole and 120 MJ/kmole, respectively. In the Knudsen regime, the intra-pellet diffusivity is much less sensitive to temperature than the two activated processes above. Therefore, an increase in sulfation temperature is expected to enhance the intra-particle concentration gradients which results in accelerated pore mouth plugging near the particle surface and thus reduced limiting conversions.

The observations concerning the effect of sulfation temperature on premature pore plugging as distinguished by pulse analysis is entirely consistent with conclusion A of section 4.2.

By reference to Figure 4.3, it is evident that the slope of $-\Delta\mu_1^{\dagger}$ versus sulfation time for low conversions increases uniformly with temperature. This slope is simply related to the rate of reaction as described by equation (4-18). Since the fixed bed does not operate in a differential mode as previously discussed, it is difficult to quantify the absolute rate of reaction at each temperature. However, the pulse-derived results are qualitatively consistent with the expectations drawn in conclusion B of the preceding section. From the pulse-derived data, it appears that rate accelerates over some period of conversion. This acceleration may be an artifact of pore volume occlusion which

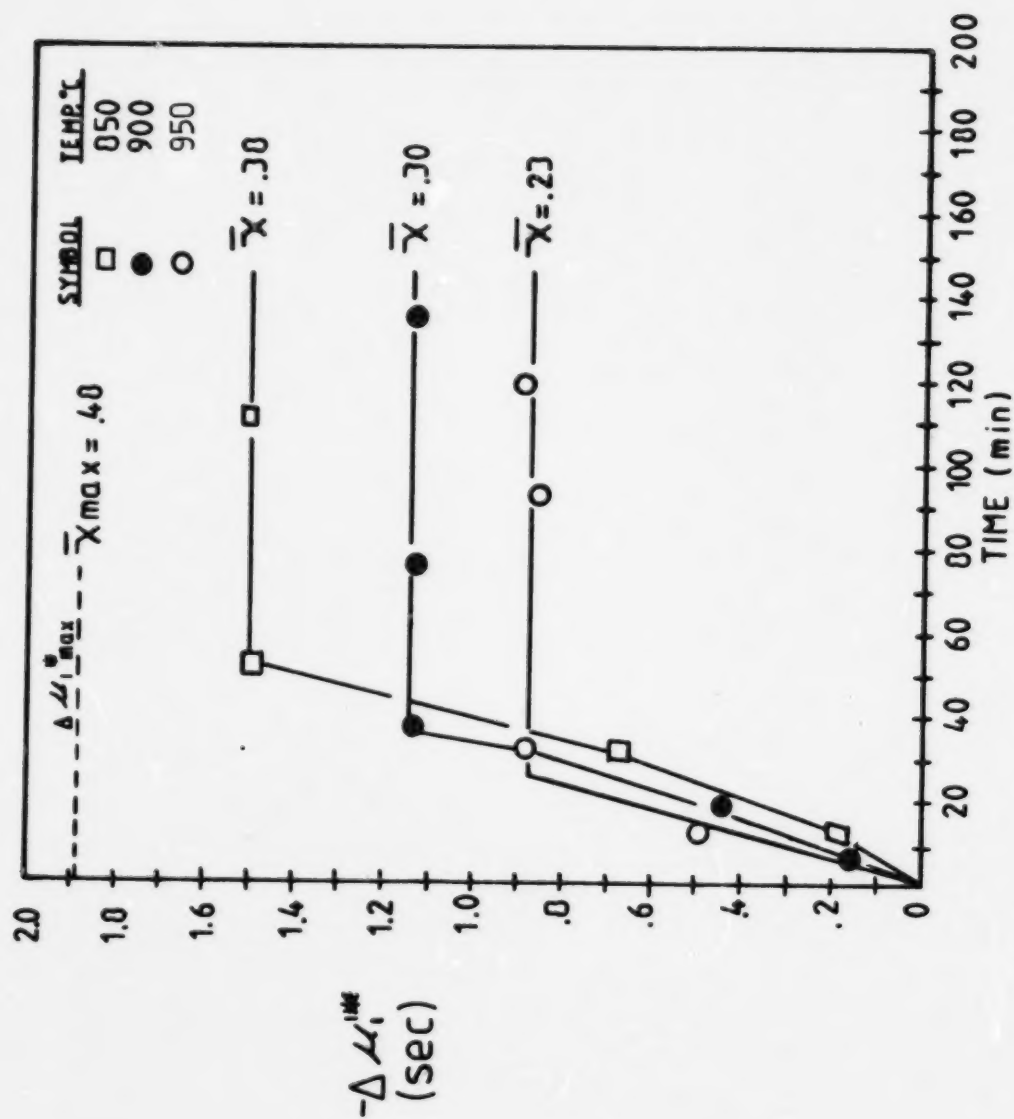


Figure 4.3 $\Delta\mu_1^*$ vs. sulfating time for Montana calcines at three temperatures for 6% SO_2 in air. 12/20 mesh.

may occur during sulfation. This occlusion would be interpreted as additional conversion, since the application of pulse data using equation (4-19) does not distinguish between reacted pore volume and occluded pore volume.

Figure 4.4 shows a plot of $-\Delta\mu_1^*$ versus sulfation time for three different SO_2 concentrations at 900°C . Increasing the concentration from 3% to 6% reduces the value of limiting conversion from .38 to .30. By analogy with the effect of temperature, increased SO_2 concentrations are expected to accelerate the rate of reaction in the vicinity of the particle surface compared to the particle interior, resulting in premature pore plugging. The pulse-derived results are again consistent with conclusion A.

Figure 4.5 shows a plot of the change in pulse variance, $\Delta\mu_2^*$, versus $-\Delta\mu_1^*$ (conversion). The resulting family of curves reveals that for each set of sulfation conditions, a different and distinct relation exists between the intra-particle mass transport and the average pellet conversion. In a previous section, it was deduced that a positive slope for this plot is indicative of increasing mass transfer resistance. At 850°C , the pulse dispersion appears to diminish throughout nearly the whole range of conversions. It is concluded that the reduction in average pellet porosity which tends to diminish pulse dispersion overshadows the increase in pulse dispersion due to enhanced mass transfer resistance.

For both concentrations at 900°C , curves similar in form although slightly shifted in the conversion variable, $-\Delta\mu_1^*$, prevail. The pulse dispersion appears to diminish initially. Near the limiting conversion (.3 and .38), a critical phenomenon concerning the intra-particle mass transport characteristics is observed. This critical phenomenon is interpreted as being associated with the value of conversion when the pores near the particle surface begin to close. Very small and perhaps undetectable changes in the average particle conversion give rise to significantly increased transport resistance. The fact that the rapidly increasing slopes of Figure 4.5 are associated with the value of $-\Delta\mu_1^*$

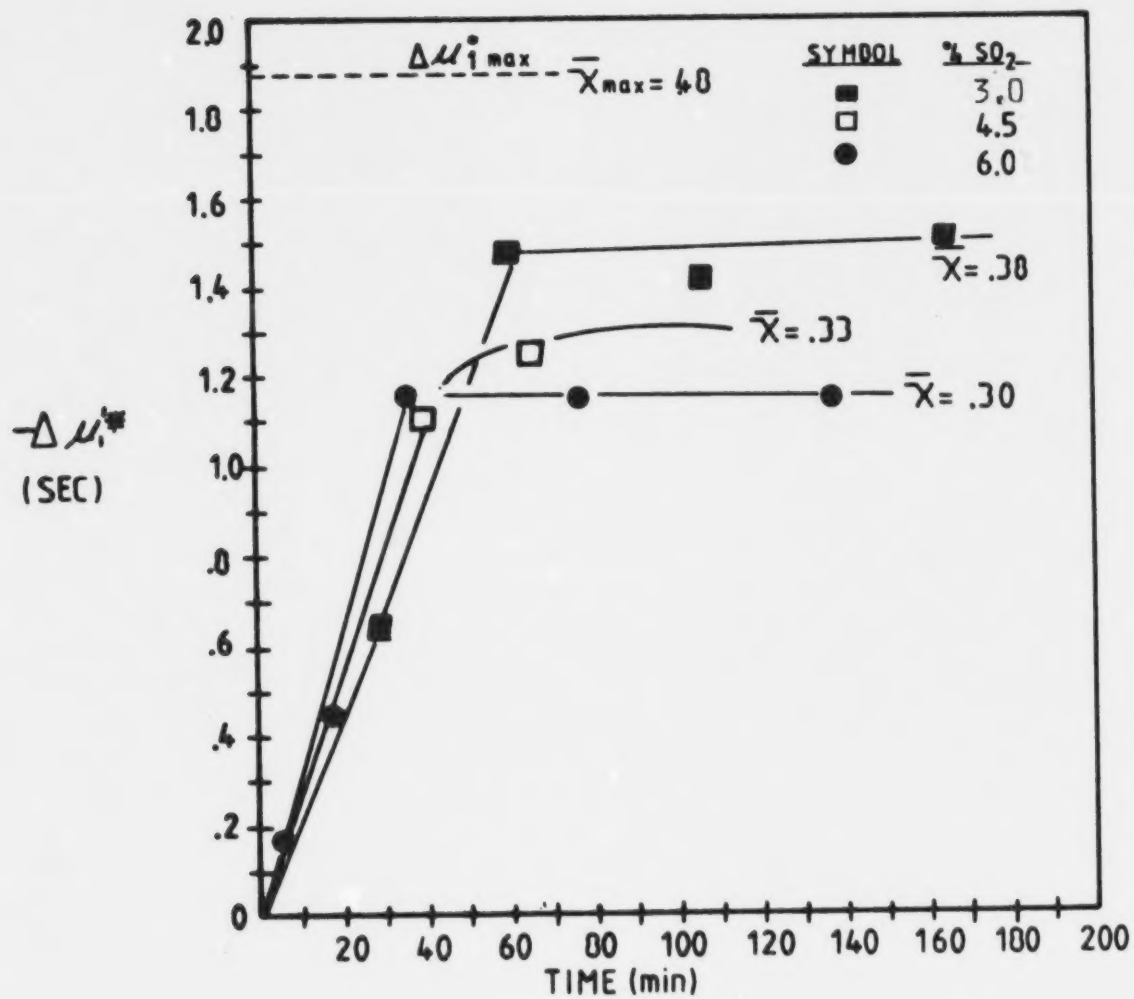


Figure 4.4 $\Delta\mu_1^*$ vs. sulfating time for Montana calcines at 900°C for three different concentrations of SO_2 in the reaction mixture

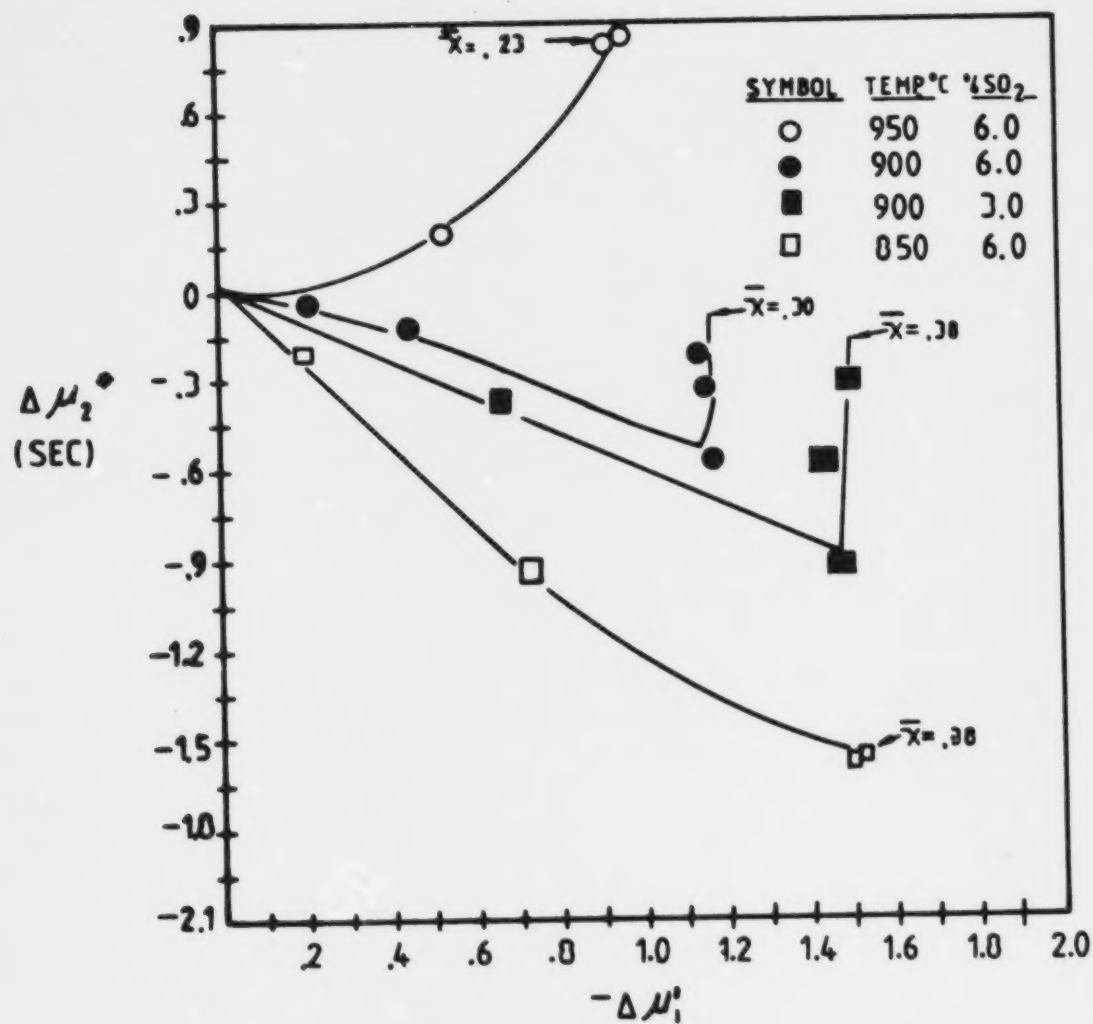


Figure 4.5 $\Delta\mu_2^*$ versus $\Delta\mu_1^*$ for sulfation of Montana calcite at different conditions: the effect of process conditions on mass transport

at which the slopes of Figure 4.3 level off provides confirming evidence concerning the role of pore plugging in the SO_2 -lime reaction.

At the highest sulfation temperature, 950°C , the pulse dispersion appears to increase for nearly all ranges of conversion. The slope is seen to rapidly increase near the limiting conversion (.23) as in the previous two cases.

The pulse-derived results are consistent with conclusion B of section 4.2. For a given level of average particle conversion, processes which accelerate the initial reaction rate will likely be reflected in increased mass transport resistances, and thus pulse dispersions.

4.6 CONCLUSIONS

The results of this investigation indicate that pulsed-gas chromatography may provide a useful tool for exploring structural and transport property transformations in reacting solid systems. The method is shown to give qualitative insight into the effect of processing conditions on these transformations. The method is shown to be adaptable to in situ, high-temperature measurements.

The pulse-derived results are consistent with the observation of previous investigators which indicates that increased temperature and SO_2 concentration enhance the initial rate of reaction but diminish the limiting conversion of the solid. The critical behavior concerning the rapidly increasing intra-particle mass transport resistance near the limiting conversion is identified from pulse data. The results reveal that, for a given level of average particle conversion, process conditions that enhance the initial rate of reaction give rise to increased mass transport resistances. The pulse-derived results in this investigation can be successfully interpreted in terms of the pore plugging models described in previous publications.

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4.8 NOTATION

A_1	= Constant defined in equation 4.16
Bi	= Modified Biot Modulus
$C(\eta)$	= Local concentration of SO_2 in lime particle.
$C(z,t)$	= Concentration of tracer at column exit
D_a	= Effective axial dispersion coefficient
D_e	= Effective intra-particle diffusivity of SO_2 in lime
D_i	= Effective intra-particle diffusivity of tracer in lime
D_i^*	= Averaged effective diffusivity of tracer in lime defined by equation 4.11
D_K	= Knudsen Diffusivity
E	= Column voidage
k_f	= Gas-to-particle mass transfer coefficient
L	= Column length
R	= Particle radius
t_s	= Sulfation time
V	= Mean interstitial carrier gas velocity
Z	= Ratio of $CaSO_4$ molar volume to CaO molar volume

4.9 GREEK NOTATION

α_i	= System constants of equations 4.19 and 4.20-23
β	= Local porosity
$\bar{\beta}$	= Average particle porosity
β_0	= Initial calcine porosity
$\Delta\bar{\beta}$	= Change in porosity due to sulfation, defined by equation 4.15
μ_1^i	= Column contribution to first absolute moment of pulse response, defined by equation 4.6

μ_2	= Column contribution to second central moment of pulse response, defined by equation 4.7
μ_1^*	= Experimentally measured first absolute moment of pulse response
μ_2^*	= Experimentally measured second central moment of pulse response
$\mu_1^*(0)$	= Measured first absolute moment of pulse response for unsulfated calcine
$\mu_{1,\text{ext}}^*$	= Extra column contribution to first absolute moment, defined by equation 4.12
$\mu_{2,\text{ext}}^*$	= Extra column contribution to second central moment, defined by equation 4.13
$\Delta\mu_1^*$	= Change in the measured first absolute moment due to sulfation
$\Delta\mu_2^*$	= Change in the measured second central moment due to sulfation
η	= Dimensionless particle coordinate
φ	= Thiele modulus for SO_2 -lime reaction
φ_{AX}	= Axial dispersion contribution to change in second central moment due to sulfation, given by equation 4-24
φ_i	= Intra-particle diffusivity contribution to change in second central moment due to sulfation, given by equation 4.25
ψ_i	= Pore or grain shape characterization factors
x	= Local conversion of lime
$\bar{x}$	= Average particle conversion
x_{max}	= Maximum theoretical lime conversion assuming complete pore volume utilization

CHAPTER 5
STUDIES OF THE RATE OF REACTION OF LIMESTONE,
LIME AND IRON-DOPED LIME WITH H_2S

5.1 OBJECTIVE

The objective of this phase was to derive the short-contact-time high-temperature rate of reaction of lime, limestone, and iron-doped lime with H_2S . We desired to use very well-characterized limestone samples, both from the physical and the chemical point of view. Therefore, several samples were carefully prepared and characterized by mercury and nitrogen porosimetry.

In addition to the classical characterization tests, we attempted to obtain the H_2S chemisorption isotherm on lime and limestone. Excessive corrosion of the pressure sensors did not allow to obtain reliable chemisorption data.

5.2 STRATEGY AND METHOD OF PERFORMANCE

Samples of Georgia Texas limestone were calcined for different lengths of time and/or different temperatures with or without iron dopant. The samples were characterized with Hg and N_2 porosimetry, NAA and H_2S chemisorption and reacted in the micro pulse differential reactor with H_2S in the reducing-zone range of temperature, i.e., 300-950°C, for contact times of the order of 10^{-2} -14 sec.

5.3 ACCOMPLISHMENTS AND RESULTS

The major accomplishments so far are:

- 1) Sixteen samples of lime or limestone were carefully prepared from Georgia Texas limestone and characterized by Hg and N_2 porosimetry.

- 2) Two units for chemisorption and surface area measurements were constructed and used for the analysis.
- 3) The pulse differential reactor was repaired and is now ready to be used for kinetic studies.

5.3.1 Samples Preparation and the Effect of Iron-Doping

Georgia Texas limestone was sieved to -120+230 mesh and calcined for 1 hr with or without predoping to different temperatures in the range of 500-1000°C. Several samples were calcined for 6 hr. Table 5.1 gives the data on the undoped limestone and Table 5.2 gives the data on the doped samples. The two most interesting features to be noted are: 1) the surface areas and pore volumes do not change much when the samples are calcined below 900°C; 2) the iron-doped samples have a larger pore volumes and surface areas than corresponding undoped samples.

Figures 5.1 to 5.8 show some of the data. Figure 5.1 demonstrates that the surface area of the calcine does not change much below 900°C for either the raw or the iron-doped limestone. However, *the iron-doped limestone begins to decompose at a lower temperature than the raw sample and its decomposition is complete in a shorter period of time. The implications of this observation to LIMB are tremendous since by changing the iron content of limestone the period of time at which all the limestone is converted to CaO can be decreased. Therefore, more of the sulfur which forms H_2S in the early stage of the reducing zone can be trapped as CaS. H_2S which is not trapped as CaS is oxidized to SO_2 and can be trapped only in the oxidizing zone, which is undesirable.*

Therefore, doping limestone with Fe^{+3} can be beneficial in particular when burning coal rich in RSH which tends to release H_2S early in the reducing zone. Such sulfur may be oxidized to SO_2 before the decomposition of undoped limestone is complete.

Figure 5.2 shows that the specific surface area of the iron-doped limestone remains larger than that of the undoped limestone even after 6 hr of calcination at 900°C. Figures 5.3 to 5.8 are sample cumulative

Table 5.1 Georgia Texas* Calcined Limestone--Undoped

Sample #	Calcination T °C	Calcination t hr	BET Surface m ² /gm	Pore Vol. ml/gm
D-Limestone	--	--	1.41	0.027
DL-1	500	1	3.00	0.020
DL-2	600	1	1.50	0.012
DL-3	700	1	2.90	0.022
DL-4	800	1	2.05	0.018
DL-5	900	1	2.15	0.014
DL-6	1000	1	7.61	0.070
DL-7	900	6	2.54	0.024

* -120+230 mesh.

Table 5.2 Georgia Texas* Calcined Iron-doped** Limestone

Sample #	Calcination T °C	Calcination t hr	BET Surface m ² /gm	Pore Vol. ml/gm
S-Limestone	--	--	2.66	0.007
SL-1	500	1	2.76	0.014
SL-2	600	1	1.98	0.015
SL-3	700	1	1.33	0.031
SL-4	800	1	3.51	0.022
SL-5	900	1	10.63	0.049
SL-6	1000	1	2.11	0.082
SL-7	900	6	14.11	0.080

*-120+230 mesh.

**About 10^{-3} mole Fe⁺³/mole Ca⁺² Applied as (NH₄)Fe(SO₄)₂ 0.1 N.

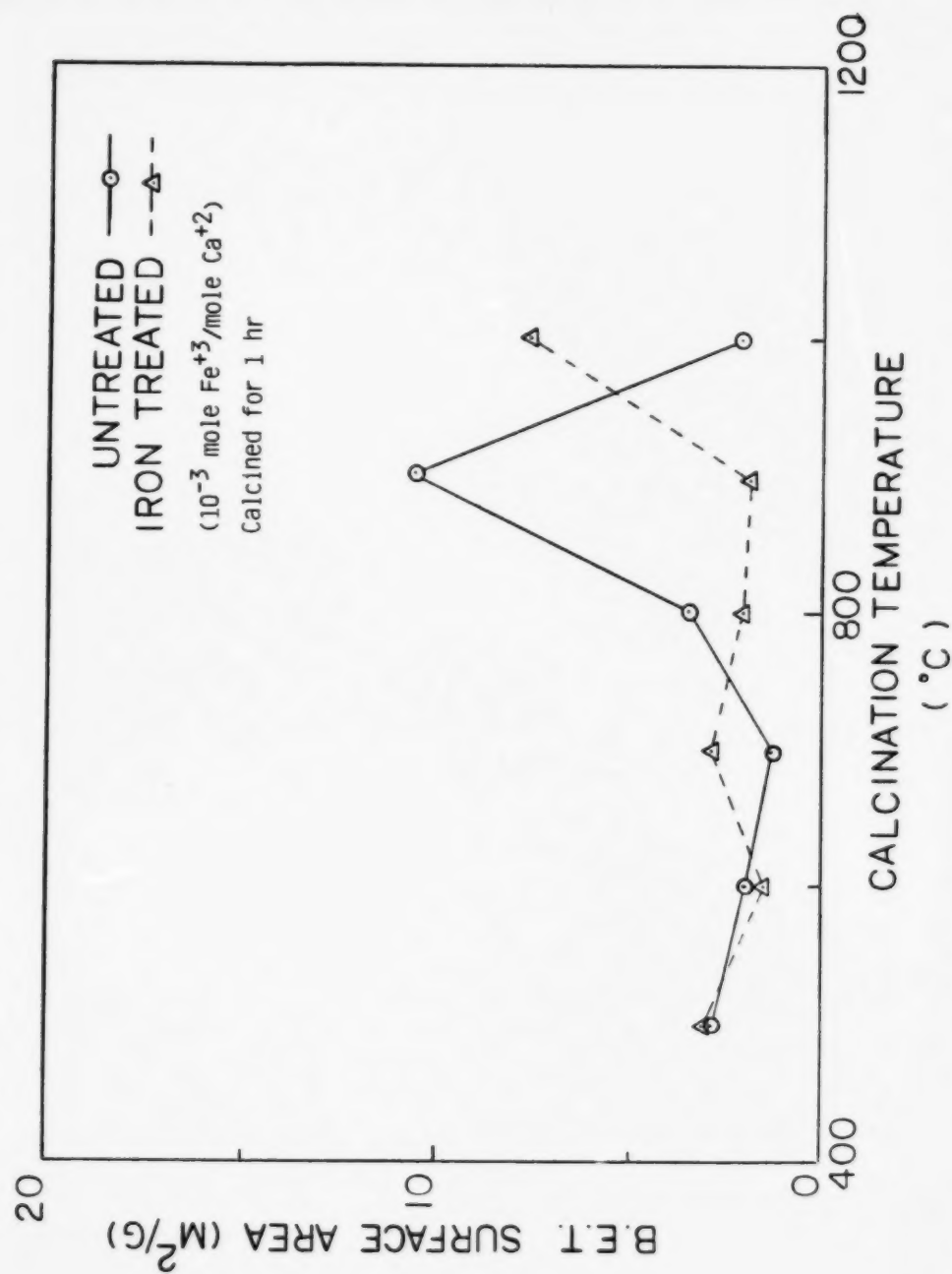


Figure 5.1 Surface areas of calcines and iron-treated calcines

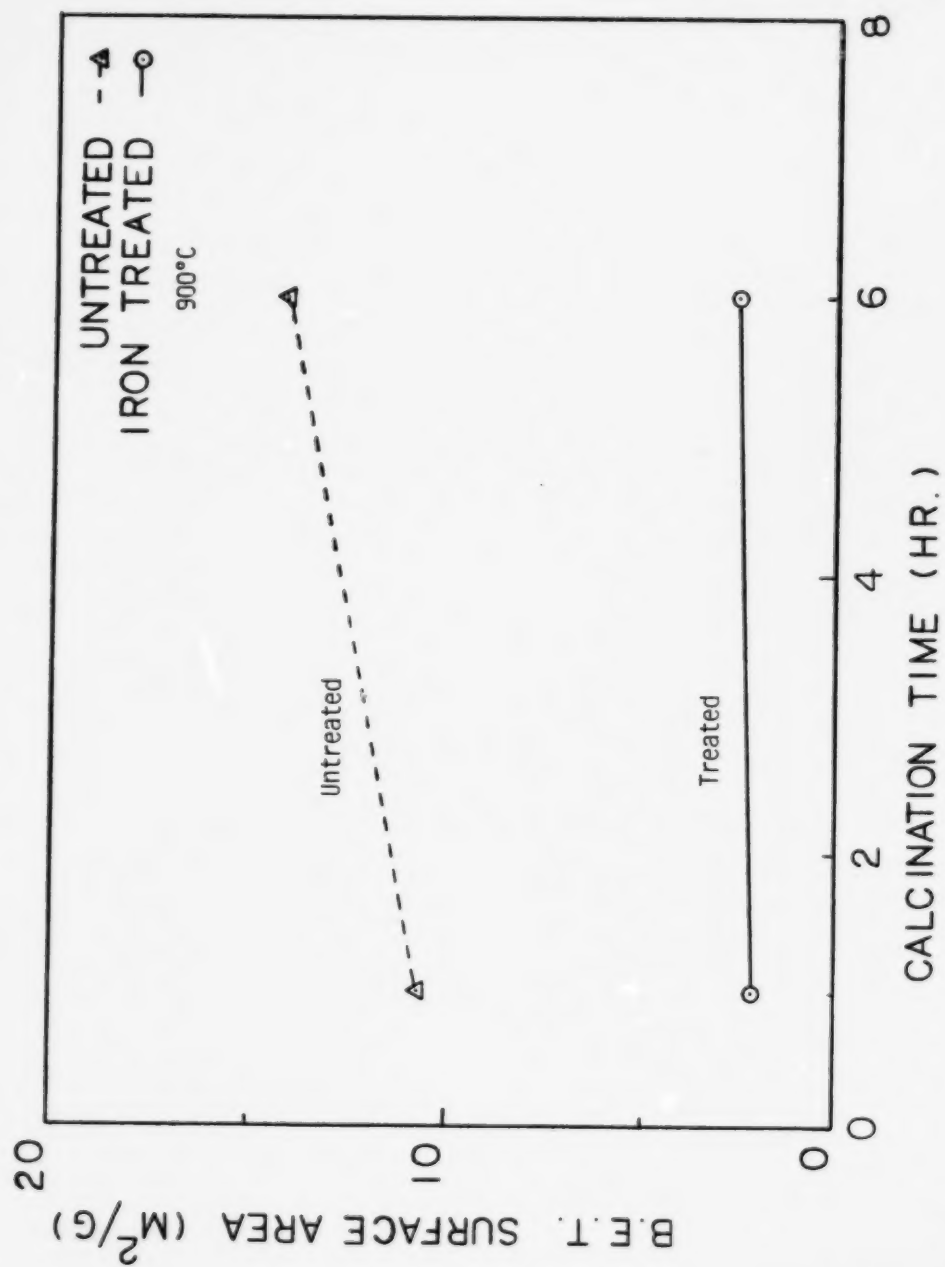


Figure 5.2 Surface areas of raw and iron-treated calcines: sintering effect

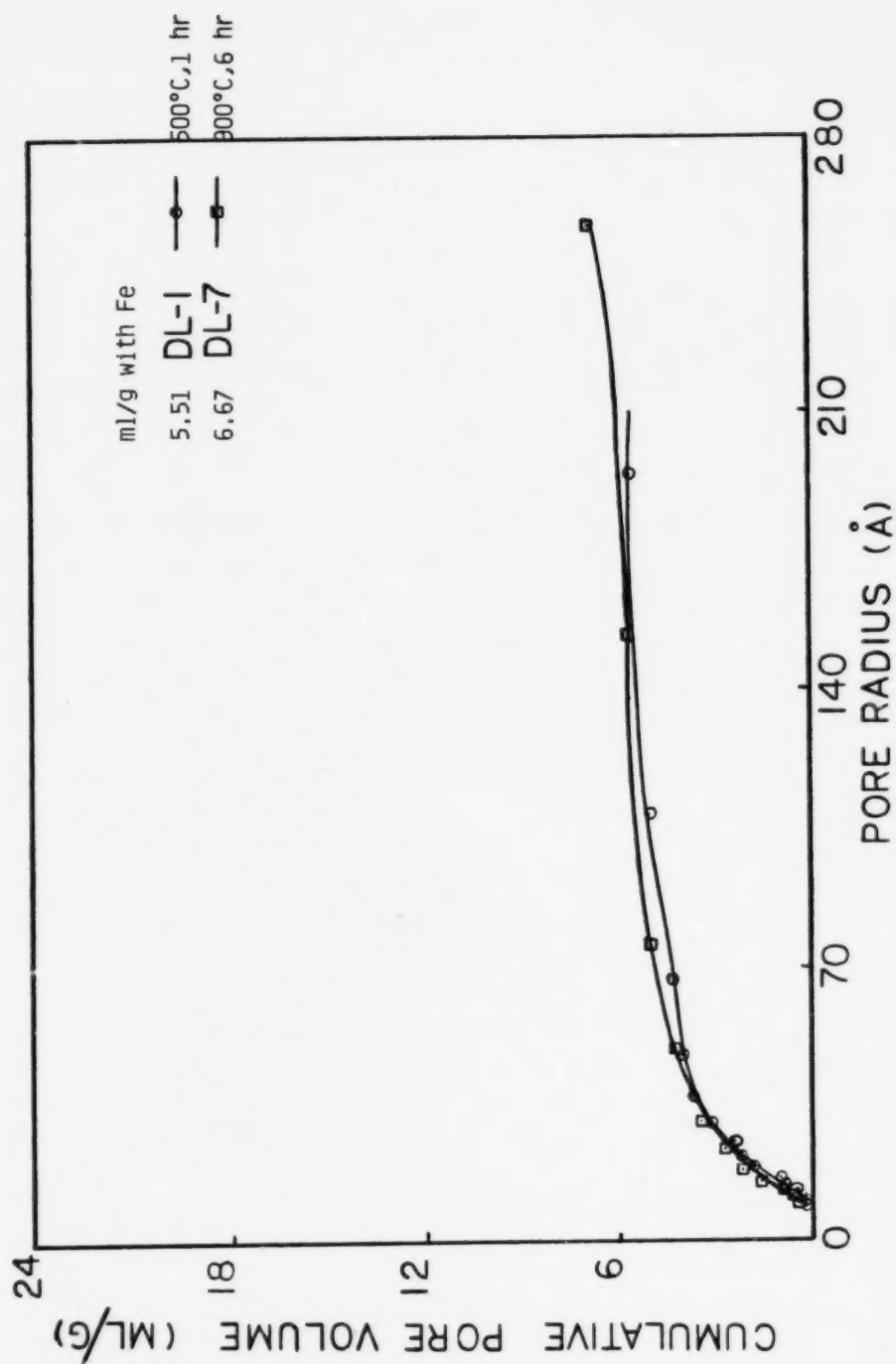


Figure 5.3 Pore volume distribution of DL-1 and DL-7

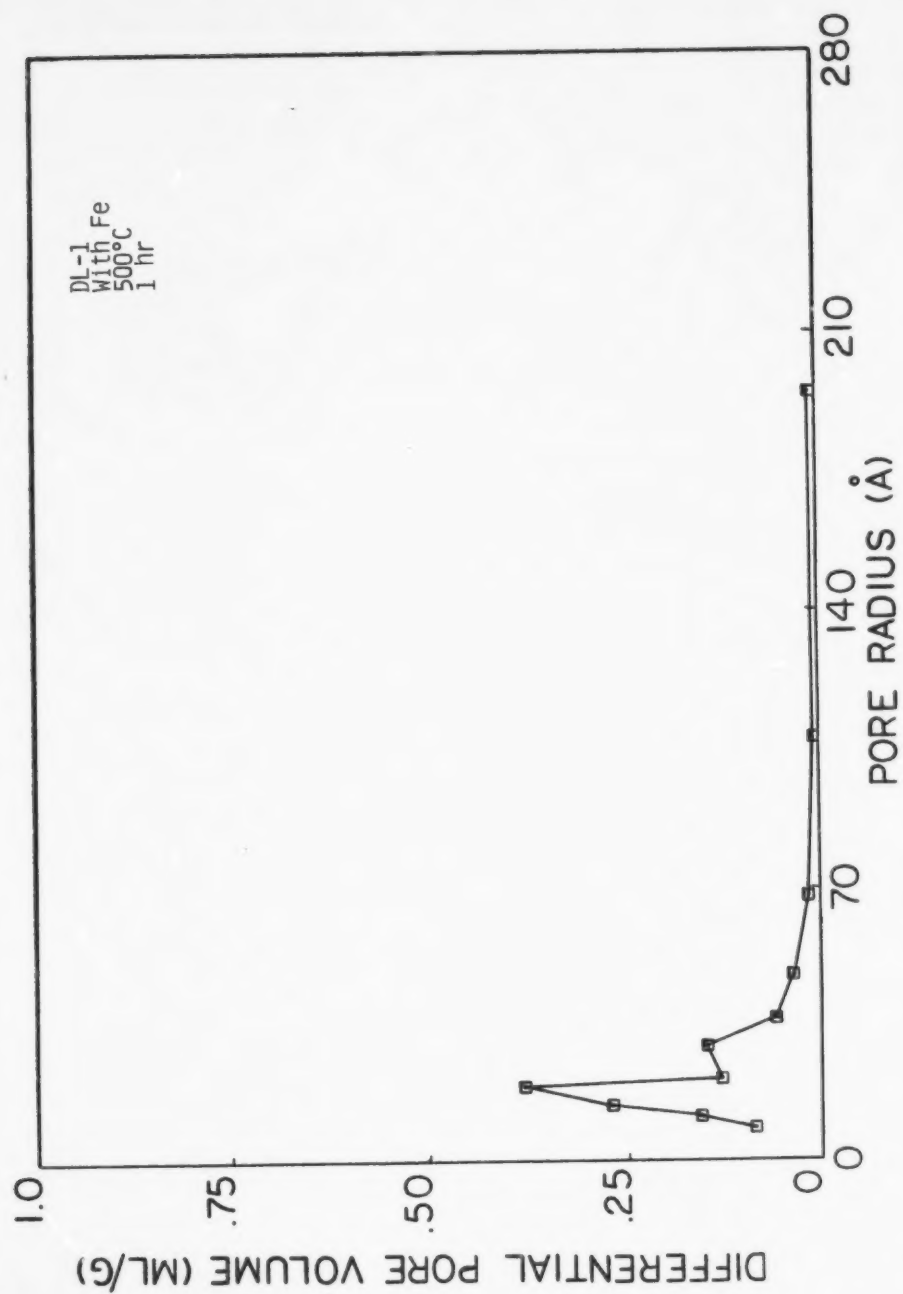


Figure 5.4 Pore size distribution of sample DL-1

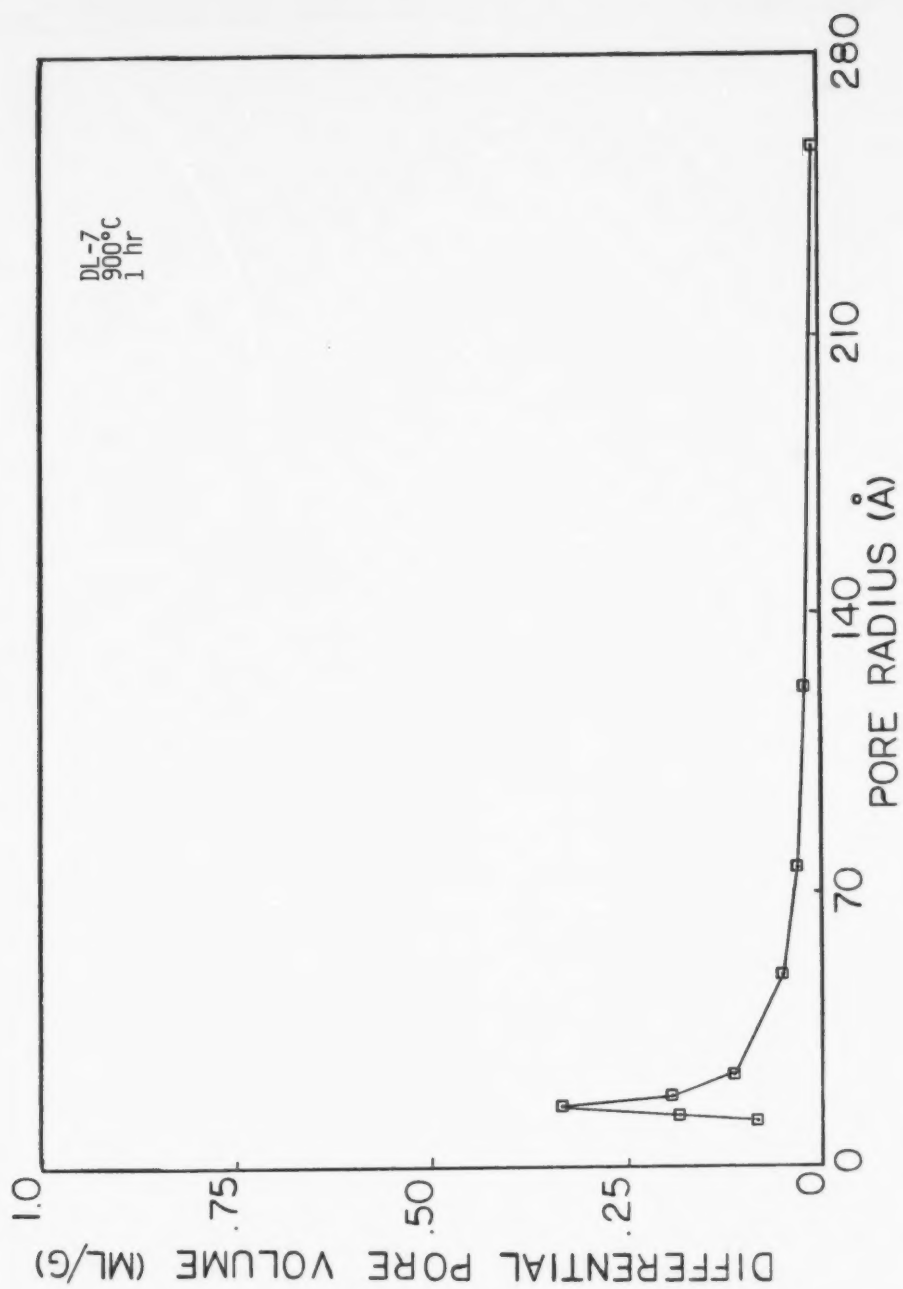


Figure 5.5 Pore size distribution of DL-7

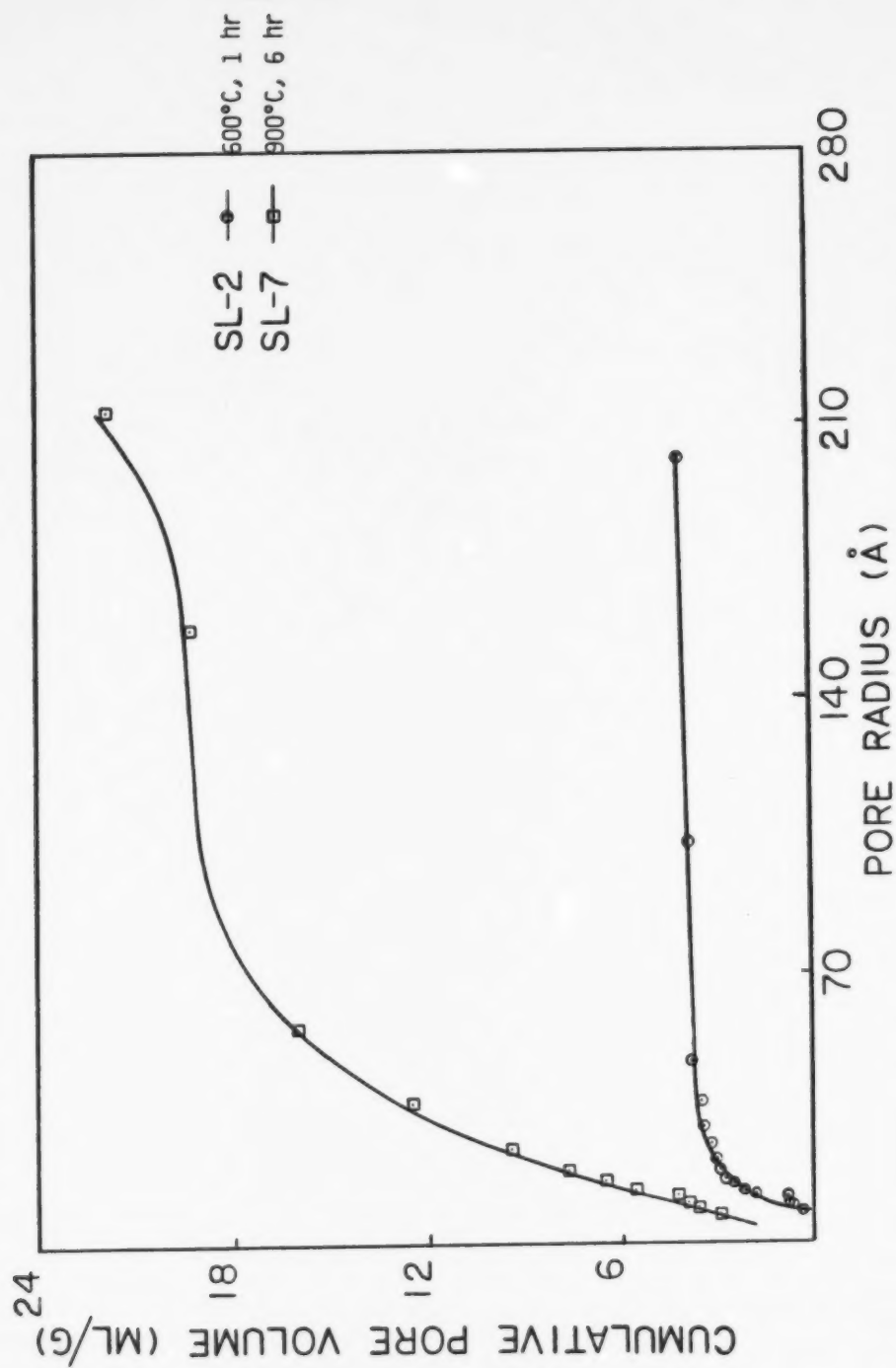


Figure 5.6 Pore size distribution of SL-2 and SL-7

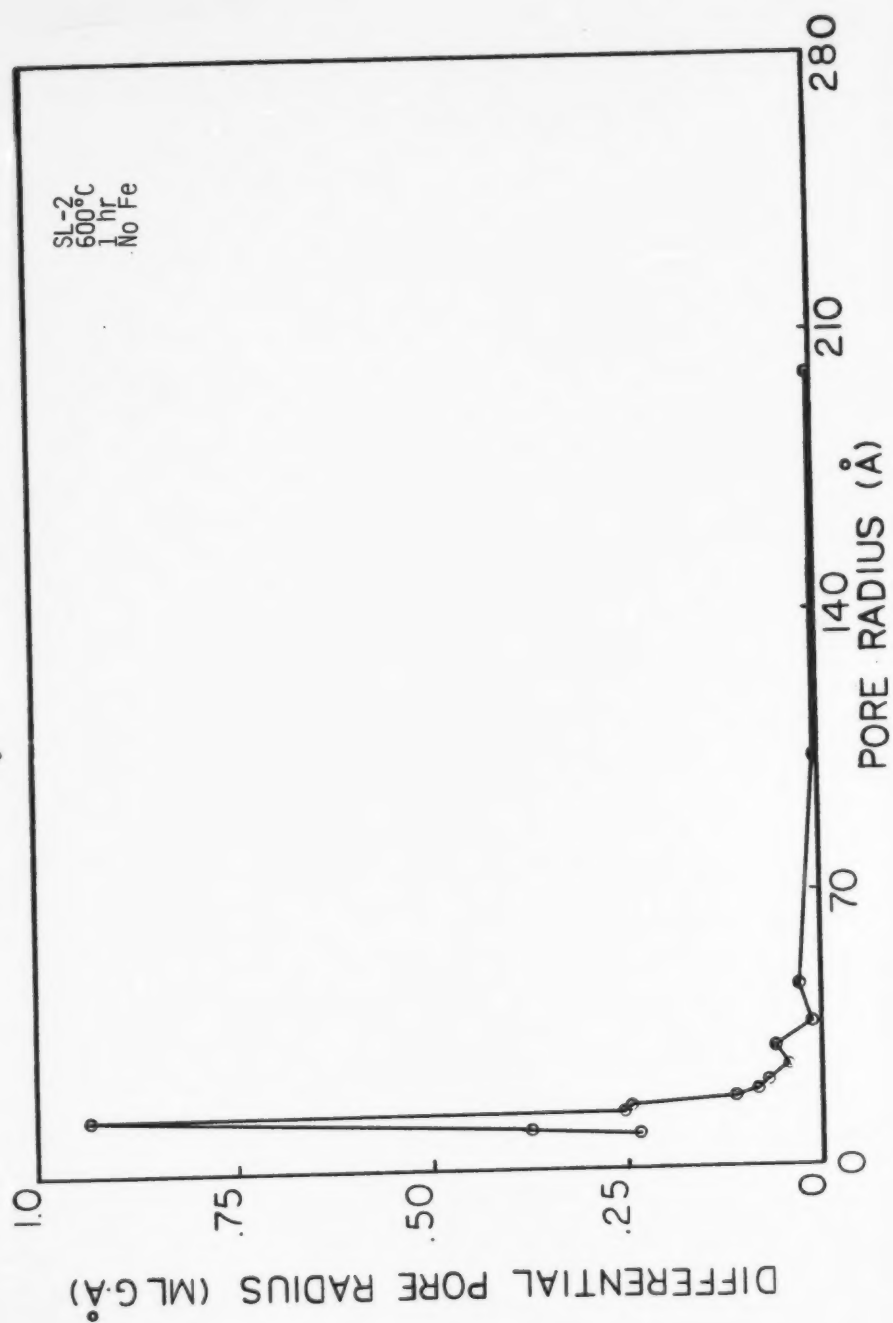


Figure 5.7 Pore size distribution of SL-2

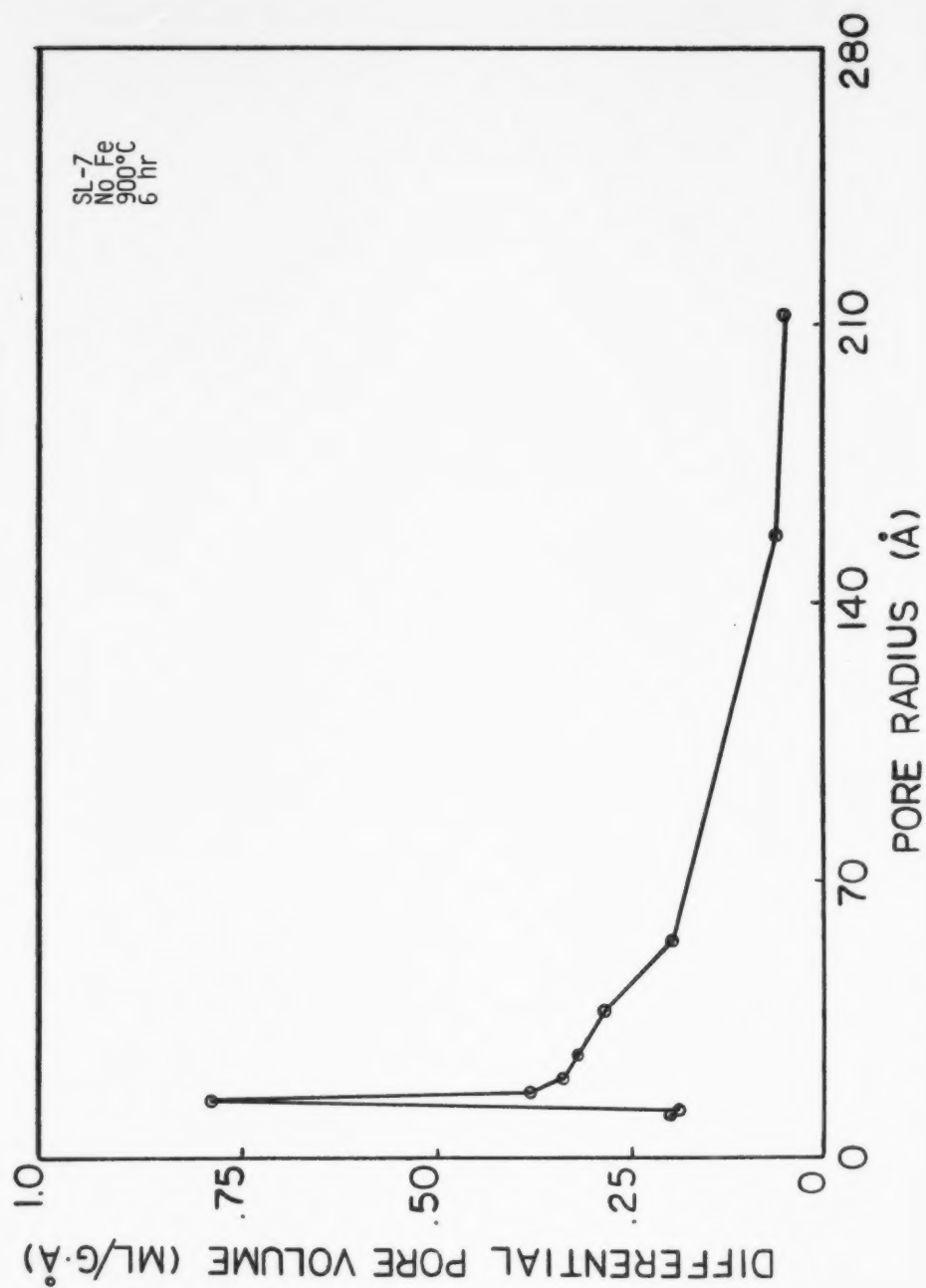


Figure 5.8 Pore size distribution of sample SL-7

and pore structure data of the many derived in the project. Tables 5.3 to 5.6 give some of the numerical values on the pore structure obtained using a computer program that we developed for this purpose.

5.3.2 Construction of Chemisorption - BET Units

In order to measure the surface area and equilibrium pore size distribution, two systems were constructed: a stainless-steel unit with a mercury manometer and a glass-quartz system with a monel transducer and a digital reader. Figure 5.9 is a schematic diagram of the system. In addition to the ordinary adsorption bulbs, special reflux-bulbs were designed, built and used to measure the adsorption isotherms of O_2 and CO_2 at boiling benzene and boiling toluene temperatures (Chap. 7).

5.3.3 Pulse Differential Reactor (PDR)

The temperature control for the PDR was not functioning and was repaired. A new micro quartz reactor (Figure 5.10) was built and tested with samples of limestone. The system was described elsewhere (A. Attar, Dev. Sci. Inst., 50(1), 111-117, 1979) and will not be described again here. See also Chapter 6.

Typically, a 100-200 mg solid sample is placed in the reactor, the reactor inserted into the furnace, and heated to the desired temperature. A stream of a carrier gas, e.g., He, N_2 , CO_2 , etc., is used to sweep the sample and pulses of the reactive gas H_2S are periodically injected into it. As proven by Attar (1979), if only a small fraction of the pulse is converted, its exact shape is not very important and the cumulative fraction reacted can be used to obtain the rate constants.

Table 5.3. Cumulative Pore Volumes

SAMPLE: DL-1		SAMPLE: DL-7	
CUMULATIVE PORE VOLUME (ml/g)	PORE RADIUS (Å)	CUMULATIVE PORE VOLUME (ml/g)	PORE RADIUS (Å)
.10	8.55	.43	9.81
.16	9.77	.55	11.20
.39	11.25	.81	12.60
.48	12.64	1.57	14.94
.91	14.20	2.15	18.02
1.00	16.09	2.70	22.75
1.82	18.27	3.37	30.73
2.17	20.99	4.22	48.28
2.41	24.50	4.93	75.27
3.12	29.14	5.66	120.93
3.55	36.02	6.67	256.32
3.98	46.99		
4.34	66.73		
4.82	107.50		
5.51	194.14		

Table 5.4. Cumulative Pore Volumes

SAMPLE: SL-2		SAMPLE: SL-7	
CUMULATIVE PORE VOLUME (ml/g)	PORE RADIUS (Å)	CUMULATIVE PORE VOLUME (ml/g)	PORE RADIUS (Å)
.25	8.20	2.92	7.43
.59	9.12	3.63	8.79
.73	10.11	3.90	10.18
.73	11.28	4.18	11.78
1.18	12.44	5.48	13.45
2.12	13.69	6.42	16.00
2.43	14.99	7.60	19.56
2.62	16.66	9.39	25.39
2.79	18.76	12.35	35.79
2.97	21.39	15.97	54.74
3.10	24.78	19.18	156.89
3.36	29.34	21.74	212.58
3.45	35.79		
3.73	45.68		
3.78	102.88		
4.05	199.64		

Table 5.5. Differential Pore Volumes

SAMPLE: SL-2		SAMPLE: SL-7	
DIFFERENTIAL PORE VOLUME (ml/g)	PORE RADIUS (Å)	DIFFERENTIAL PORE VOLUME (ml/g)	PORE RADIUS (Å)
.23	8.20	.19	10.18
.91	9.11	.18	11.78
.93	12.44	.78	13.45
.25	13.69	.37	16.00
.24	14.99	.33	19.56
.11	16.66	.31	25.39
.08	18.76	.28	35.79
.07	21.39	.19	54.74
.04	24.78	.06	156.89
.06	29.34	.05	212.58
.01	35.79		
.03	45.68		
.001	102.88		
.003	199.64		

Table 5.6. Differential Pore Volumes

SAMPLE: DL-7		SAMPLE: DL-7	
DIFFERENTIAL PORE VOLUME (ml/g)	PORE RADIUS (Å)	DIFFERENTIAL PORE VOLUME (ml/g)	PORE RADIUS (Å)
.09	8.55	.08	11.20
.16	11.25	.18	12.60
.27	14.20	.33	14.94
.38	18.27	.19	18.02
.13	20.99	.11	22.75
.15	29.14	.08	30.73
.06	36.02	.05	48.28
.04	46.99	.03	75.27
.02	66.73	.02	120.93
.01	107.50	.01	256.32
.01	194.14		

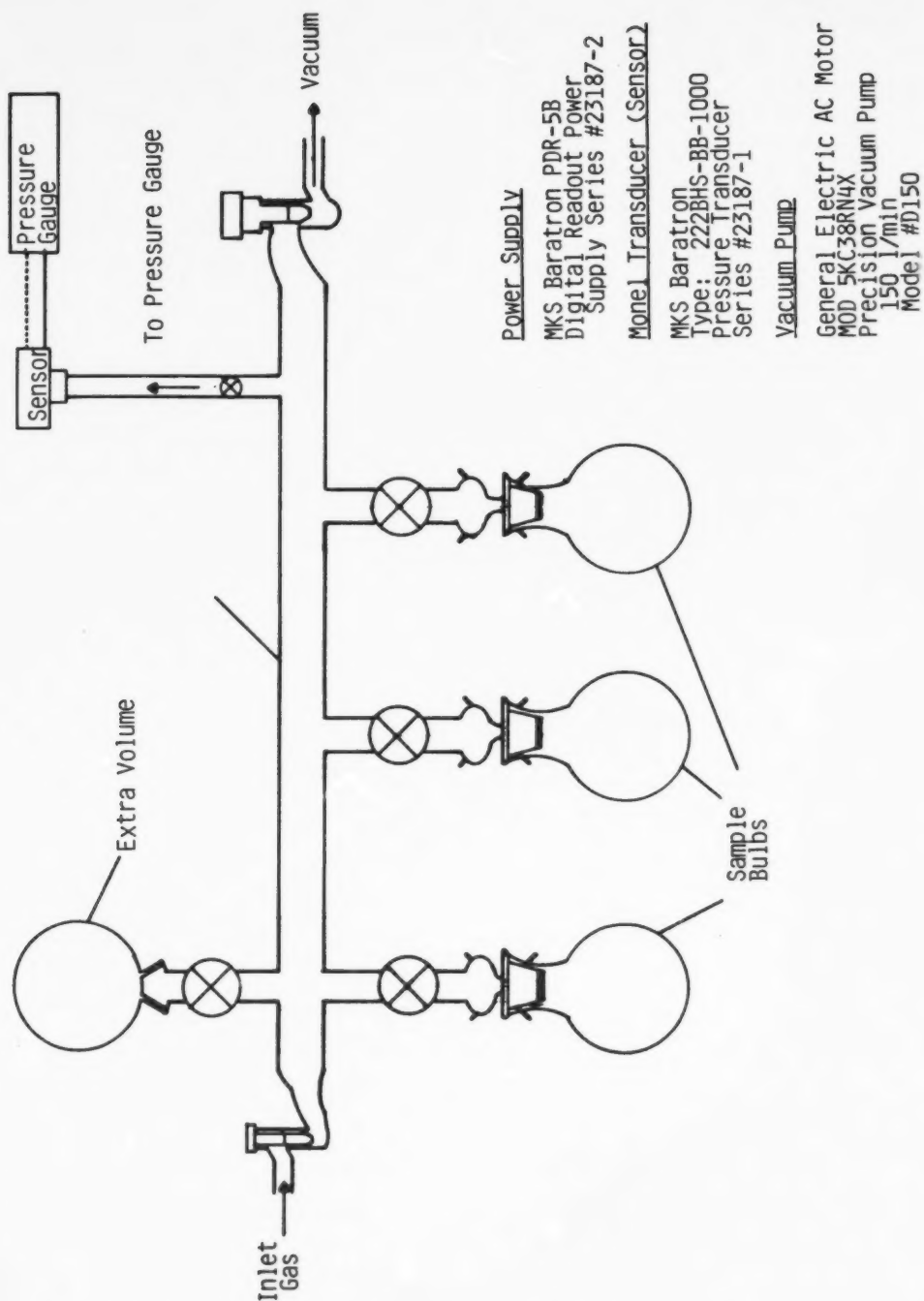


Figure 5.9 Glass-quartz pore structure and chemisorption unit

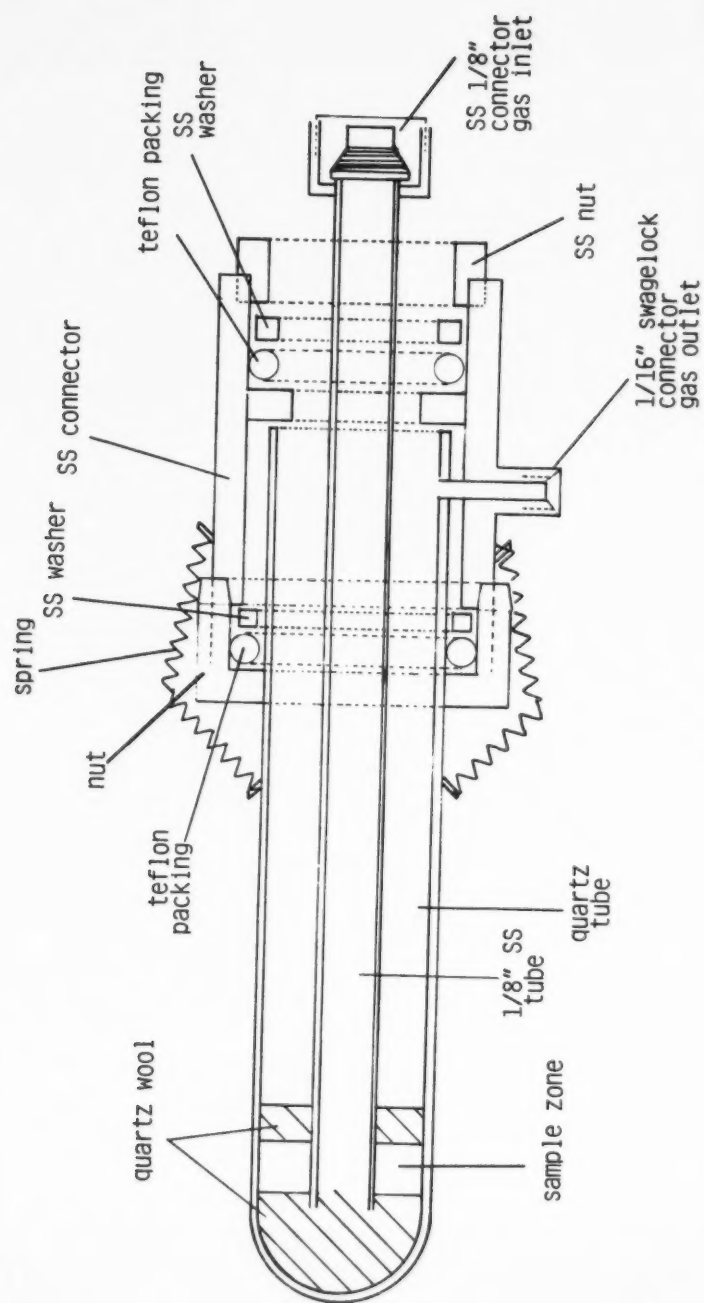


Figure 5.10 Quartz PDR

CHAPTER 6

REDUCTION OF IRON PYRITE (FeS_2) WITH HYDROGEN

One of the sources of hydrogen sulfide (H_2S) in the initial stages of LIMB, i.e., in the reducing zone, involves the reduction of some of the coal iron pyrite, FeS_2 , to H_2S and pyrrhotite, FeS .



The reduction is complete in 3-5 min at 700°C ; ~~however~~, it begins much earlier and is detectable at temperatures as low as 300°C . Since early-formed H_2S may not have the opportunity to react with CaO , and since the CaCO_3 may not have fully decomposed yet, it was desirable to obtain kinetic data on the rate of reduction of FeS_2 with hydrogen at low temperatures.

6.1 OBJECTIVES

The main objectives of this task were to derive data on the mechanism and rate of reduction of FeS_2 with H_2S in the temperature range of 300 - 400°C .

6.2 BACKGROUND

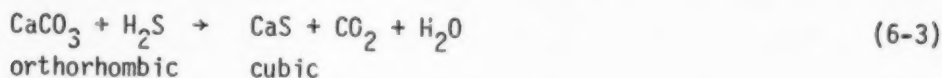
Since the reduction of FeS_2 involves the formation of a new solid phase, the FeS , from the old solid FeS_2 , it was decided to examine the mechanism in a slightly more general manner, i.e., from the point of view of the variables which control a general phase transformation in gas solid reaction. Some of the work was presented recently in the Los Angeles meeting of the AIChE and a modified version of that paper is given here.

6.3. INTRODUCTION

Gas-solid reactions of the type



are common in the chemical industry, yet some aspects of their kinetics have received little attention. Conversion of a solid to another solid always involves phase change since the crystalline structure of the solid product C cannot be the same as that of the solid reactant A. Two examples are:



and:



As shown, the chemical reaction may change the crystalline structure and/or the atomic spacing, as expressed by a change in the molar volume.

Phase changes due to gas-solid chemical reactions differ from ordinary phase changes in several ways:

- 1) They involve surfaces on which a gas-solid reaction can occur, and
- 2) gaseous reactants and/or products have to be able to reach the surface, most likely by diffusion.

Research on the kinetics of gas-solid reactions is often complicated by the surface heterogeneity and by the local thermal effects of the reaction. When the chemical reaction takes place on the active surface site, the heat of the reaction accelerates the local reaction rate. Traditional chemical reaction engineering has addressed gas-solid reactions as a process in which the thermodynamically stable solid product C is formed instantaneously when the solid A reacts with the gas

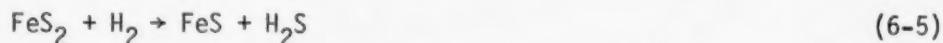
B. However, the actual sequence consists of the following steps:

1) formation of a quantity of a solid with the stoichiometry of the solid C but with a steric arrangement similar to that of A; 2) nucleation of the new phase of the thermodynamically stable solid C and, 3) growth of the nuclei to form additional thermodynamically stable solid C.

As an example, Attar and Dupuis (1979) (1) have shown that when CaCO_3 (orthorhombic) reacts with H_2S at temperatures below 634°C , an impermeable layer of material, with the stoichiometry CaS is formed on the CaCO_3 surface which blocks the reaction of additional H_2S with the solid. When this material is heated above 634°C , a new phase nucleates on the surface of the orthorhombic CaCO_3 and the gas-solid reaction proceeds as one would expect from a gas-solid reaction. This system is not unique, of course, and a phase transition has to occur in any gas-solid reaction with a solid product. Sometimes the mechanistic steps are important and distinguishable; however, in many cases the reaction temperature is sufficiently high that the new phase nucleates essentially instantaneously. Two mechanisms for a phase change can be proposed: random nucleation on a clean surface and nucleation on surface defects. When a relatively defects-free solid surface reacts with a gas, some of the surface ions may be replaced by analogous ions which subsequently may rearrange to form the stable new solid. For example, in the case of reaction (6-3), the $\text{CO}_3^{=}$ ion may be replaced by an $\text{S}^{=}$ ion. The product will have the stoichiometry CaS but the crystalline structure of the original material, i.e., the CaCO_3 . When a sufficient number of $\text{CO}_3^{=}$ ions are replaced by $\text{S}^{=}$, the new phase of cubic CaS may nucleate if the random movements of surface ions become sufficiently large to allow a sufficient number of them to rearrange and reach the critical size nuclei (1). Since the diffusivity of ions in solid depends on the temperature according to Arrhenius, an increase in the temperature will enhance the rate of phase transition. Once the nuclei of the new phase are formed, they will grow by adding newly formed reaction products.

When a surface with defects is reacted, the reaction products will accumulate around the defects and a clear nucleation step may not be detectable.

After nucleation has occurred, the newly formed nuclei grow by adding material. The rate of their growth may be limited by the rate of gas-phase mass transfer, by the rate of the surface chemical reaction or by the rate of diffusion through a layer of products. *The chemical reaction may proceed on the unreacted surface between the newly formed nuclei, or on the perimeter of the new nuclei. In the case of the reduction of FeS₂ crystals, the reaction appears to proceed on the circumference of the nuclei.* The rate of the reaction



was studied by many investigators; some of them are listed in Table 6.1. All these studies concentrated on the kinetics of the post nucleation stage. The main conclusions from these studies are:

- 1) Reaction (6-5) commences in the temperature range of 300-450°C and a complete conversion of the FeS₂ to FeS is feasible within "reasonable" laboratory-scale time.
- 2) Complete desulfurization of the FeS is possible only above about 800°C.



- 3) The activation energy for reaction (6-5) is in the range of 20-35 kcal/mole.
- 4) The rate limiting step of reaction (6-5) is either the rate of migration of S⁼ or S₂⁼ in the solid or the rate of diffusion in the product layer of FeS. In this work, the initial stages of reaction (6-5) were studied in order to obtain information on the nucleation of FeS crystals and the mechanism of their growth before they coalesced.

6.4 EXPERIMENTAL

The experimental system (Figure 6.1) was described in detail by Attar (1979) (2) and will be covered here only very briefly.

The experimental system consists of four major components: (1) a differential reactor, (2) a pulse injector, (3) a gas chromatograph with a TC detector, and (4) an integrator with a data system.

TABLE 6.1 SUMMARY OF THE PUBLISHED LITERATURE ON THE KINETICS OF REACTIONS OF IRON PYRITE

Type of data	Method	Temp. range (°C)	Gas	Major emphasis	Ref.
Review				Review of literature to 1978	3
Kinetics	DTA, DSC	300-900	N ₂ , He, H ₂	Kinetics of reaction	4
Phase transition	DTA	320-600	With and without air, H ₂ O	Phase transition. Type of products	5
Phase transition conversion vapor pressure	Fixed bed flow reactor	400-1200	Air, steam, CO, CO ₂ , H ₂ , coal-gas	Type or products. Conversion at different temperatures	6
Vapor pressure conversion	Fixed bed closed reactor	500-800	CO ₂	Conversion	7
Vapor pressure conversion phase behavior	Fixed bed	600-1055	Vacuum	Detailed vapor pressure characteristics of FeS ₂ from different locations	8
Weight loss	TGA	100-1100	Unspecified	Temperature of maximum rate of weight loss	9
Phase diagram of FeS	DTA, sealed cell	800-1200	Inert	Melting and decomposition temperatures	10
Phase transitions	DTA	300-1000	H ₂ O, N ₂ , O ₂	Effect of type of gas and rate of heating	11
Phase transition type of products	DTA	500-1000	Air, inert	Effect of particle size, and heating rate on transition temperatures and products	12

TABLE 6.1 (CONTINUED)

Type of data	Method	Temp. range (°C)	Gas	Major emphasis	Ref.
Transition temp.	Magnetization and demagne- tization	50-700	O ₂	Effect of particle size on the rate of oxidation	13
Rate of oxidation		650 (?)	O ₂	Particle sintering. Rate of de- composition and oxidation. Kinetic model	14
Free energies		300-1000	H ₂ , O ₂	Free energy estimates for the major reactions	15
Equilibrium constants		630-1030	H ₂	Equilibrium between H ₂ and FeS ₂	16
Rate of decomposition	TGA	400-670	Vacuum N ₂	Rate data. Kinetic model	17
Kinetic	TGA	400-700	O ₂ , CO ₂ , H ₂	Effect of type gas and temperature on the rate of decomposition. Kinetic model	18
Kinetic	Temperature programmed, mass spec- trometry	300-1300	H ₂	Activation energy and frequency constants	19
Kinetics	Differential reactor	300-600	H ₂	Activation energies, impurities	20

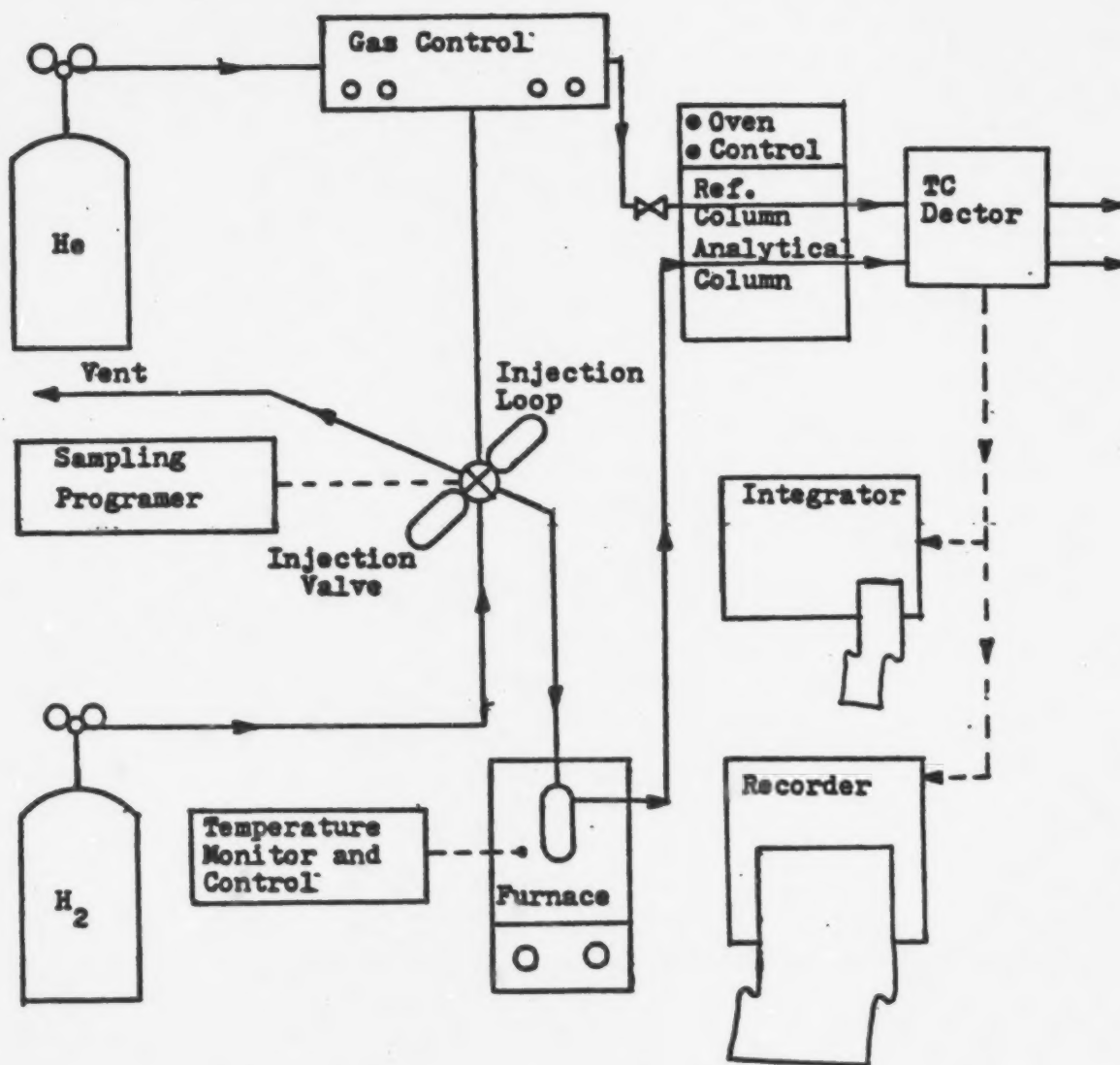


Figure 6.1 Schematic diagram of the experimental system

The reactor is inserted through the wall of a high-temperature furnace in which temperature is controlled and monitored.

Pulses of the hydrogen are fed using a microprocessor controlled gas-chromatograph injector. The size of the injector loop determines the size of the pulse of hydrogen which is introduced into the stream of carrier gas (CG). The CG, helium in this case, is passed through the reactor and into a chromatographic column and detector.

Each pulse of hydrogen, which is injected into the reactor, results in a pulse which consists of the reaction products plus the unreacted hydrogen. The mixture of gases is separated on the column and detected by the TC detector. The signal from the detector is integrated by a microprocessor which multiplies the areas by the proper calibration factors and prints the amounts of each component in the pulse of products of the reaction. The integrator and the injector are synchronized so that periodic operation is possible. The repeatability of the injections was 0.05% or better. The overall accuracy of the analysis was at least 10% and usually better than 2% based on material balance.

Mixtures of H_2S and H_2 were separated on a 1.83 m x 3.2 mm column of Chromosorb 105 80/100 mesh at 46°C. The helium flow was 75 ml/min.

The pyrite that was tested was purchased from Fisher Scientific.

The advantage of using the pulse technique for this is that it allows the introduction of extremely small amounts of reactant gas to the surface, at realistic temperatures and pressures and still the ability to follow the kinetics of the reaction. In many classical experimental systems, the surface undergoes very severe changes in the initial period of the reaction which mask the effect of the nucleation and initial growth of the new phase.

The iron pyrite was prepared for reaction as follows:

- 1) The pyrite was ground and sieved to -120 mesh +170 mesh.
- 2) The pyrite was then washed at 25°C in concentrated HCl.
- 3) Washed with H_2O which had been boiled to drive off dissolved oxygen.
- 4) Dried in vacuum oven for four hours at 70°C.
- 5) Rinsed with CCl_4 to remove organics.

- 6) Returned to vacuum oven for 30 minutes.
- 7) Stored under N_2 in sealed flask.

The experimental run was carried out by the following procedure:

- 1) A dry empty 1/4" x 2 ft S.S. reactor was weighed and its exact length measured.
- 2) Pyrite was charged into the reactor and the reactor reweighed; then the net weight of pyrite was calculated.
- 3) The reactor was connected to the gas inlet and outlet lines in the furnace.
- 4) The furnace temperature was brought to 375°C and held for one hour.
- 5) The furnace temperature was set at the desired operating temperature and allowed to equilibrate.
- 6) Carrier gas and reference stream gas flow rates were measured using a soap film gas flow measuring device.
- 7) Pulsing was initiated and controlled by the microprocessor.
- 8) Carrier gas and reference stream flow rates were measured periodically during run.

Actual experimental runs were carried out at 300°C, 315°C, 350°C, and 375°C.

Table 6.2 summarizes the run conditions. The results shown in Table 6.2 were obtained using H_2 pulses of about $6 \cdot 10^{-5}$ moles. Calibration of the detector and the integrator have shown that the response factor is $2.1047 \cdot 10^{10}$ counts/mole H_2S . Typical usable integration counts are in the range of 200- 10^5 counts. The response was linear in this range. Material balances on pulses were closed within $\pm 5\%$.

6.5 RESULTS AND DISCUSSION

A summary of the results of reacting FeS_2 with hydrogen at different temperatures is given in Table 6.3. The results are plotted in Figure 6.2. Note that the 350°C run was on FeS_2 from a different batch. The data can be interpreted in several ways as described in Table 6.4. For reasons explained by Attar (1979) (2) the reaction was assumed to be isothermal.

TABLE 6.2 CONDITIONS OF RUNS

T°C	Grams FeS ₂	Column length (cm)	Gas flow rate (cm ³ /sec)	Gas velocity (cm/sec)*	FeS ₂ treatment
300	16.6	36	0.50	1.58	a.
315	16.0	34	0.69	2.18	a.
350	16.3	35	0.58	1.83	a, b
375	16.6	36	0.58	1.83	a.

*Based on empty tube cross-section.

- a. 1) Pyrite was ground and sieved to -120 mesh +170 mesh.
- 2) Washed at 25°C in concentrated HCl.
- 3) Washed with DI H₂O which had been boiled to drive off oxygen.
- 4) Dried in vacuum oven for four hours at 70°C.
- 5) Rinsed with CCl₄ to remove organics.
- 6) Returned to vacuum oven for 30 minutes.
- 7) Stored under N₂ in sealed flask.
- b. A different batch of FeS₂ was used in this run.

TABLE 6.3 RESULTS OF RUNS AT 300, 315, 350 AND 375°C

Pulse Number	300°C		315°C		350°C		375°C	
	A(I)	A _S (I)	A(I)	A _S (I)	A(I)	A _S (I)	A(I)	A _S (I)
5	232.	249.	3972.	3892.	27889.	34920.	22515.	23915.
10	257.	279.	4103.	4236.	52760.	54769.	25780.	26965.
15	291.	291.	4521.	4631.	60925.	61835.	27792.	28054.
20	315.	329.	5068.	5260.	65351.	66030.	28994.	29190.
25	321.	344.	5820.	5946.	69407.	70045.	29777.	29955.
30	351.	362.	6554.	6682.	73998.	75580.	30567.	30754.
35	400.	400.	7205.	7607.	82508.	84332.	31220.	31494.
40	378.	409.	8679.	8801.	91547.	93113.	32227.	32150.
45	418.	423.	9166.	9265.	98139.	98994.	32507.	32744.
50	444.	435.	9605.	9669.	101880.	102206.	33166.	33162.
55	472.	476.	9971.	10095.	103129.	103385.	33421.	33416.
60	471.	491.	10364.	10433.	103250.	103398.	33521.	33682.
65	489.	495.	10683.	10712.	103518.	103630.	33742.	33810.
70	507.	500.	10866.	10910.	102894.	102835.	33843.	33813.
75	540.	535.	11068.	11132.	103846.	103071.	34310.	34079.
80	547.	557.	11247.	11314.	101803.	101620.	33998.	34103.
85	582.	580.	11519.	11603.	101129.	100840.	33799.	33757.
90	588.	582.	11706.	11692.	110287.	100150.	33774.	33649.
95	616.	611.	11843.	11846.	99377.	99112.	33565.	33597.
100	638.	530.	12040.	12015.	98418.	98163.	33232.	33167.
105	645.	644.	12041.	12067.	97053.	96953.	35169.	33103.
110	646.	646.	12133.	12185.	96268.	96323.	33116.	33055.
115	666.	661.	12384.	12307.	95943.	95538.	33192.	33050.
120	680.	227.	12351.	12366.	94517.	94317.	32802.	32799.
125			12469.	12495.	93610.	93614.	32656.	32611.
130			12492.	12536.	92884.	92770.	32576.	32456.
135			12523.	12576.	92548.	92343.	32398.	32276.
140			12656.	12649.	91470.	91478.	32305.	32230.
145			12740.	12762.	91026.	91009.	31949.	31920.
150			12806.	12825.	90743.	90700.	31980.	31977.
155			12852.	12835.	89015.	88995.	31567.	32213.
160			12854.	12879.	88920.	88900.	31819.	31748.
165			12968.	12915.	88820.	88812.		
170			12998.	13009.	86967.	87777.		
175			13119.	12984.	88477.	88331.		
180			13082.	13079.	87689.	87775.		
185			13059.	13108.	87244.	87176.		
190			13112.	13065.	86898.	86733.		
195			13238.	13209.	86401.	86243.		
200			13199.	13207.				
205			13131.	13154.				
210			13242.	13250.				
215			13365.	13329.				
220			13387.	13309.				

TABLE 6.3 (CONTINUED)

Pulse Number	300°C		315°C		350°C		375°C	
	A(I)	A _S (I)	A(I)	A _S (I)	A(I)	A _S (I)	A(I)	A _S (I)
225			13309.	13334.				
230			13226.	13325.				
235			13433.	13302.				
240			13473.	13234.				
245			13345.	13358.				
250			133454.	13355.				
255			13580.	13405.				
260			13331.	13329.				
265			13378.	13343.				
270			13463.	13443.				
275			13275.	13348.				
280			13408.	13380.				
285			13263.	13399.				
290			13320.	13368.				

A(I) = Actual area of integrated pulse; counts

A_S(I) = Smoothed area = [A(I) + A(I + 1) + A(I + Z)]/3

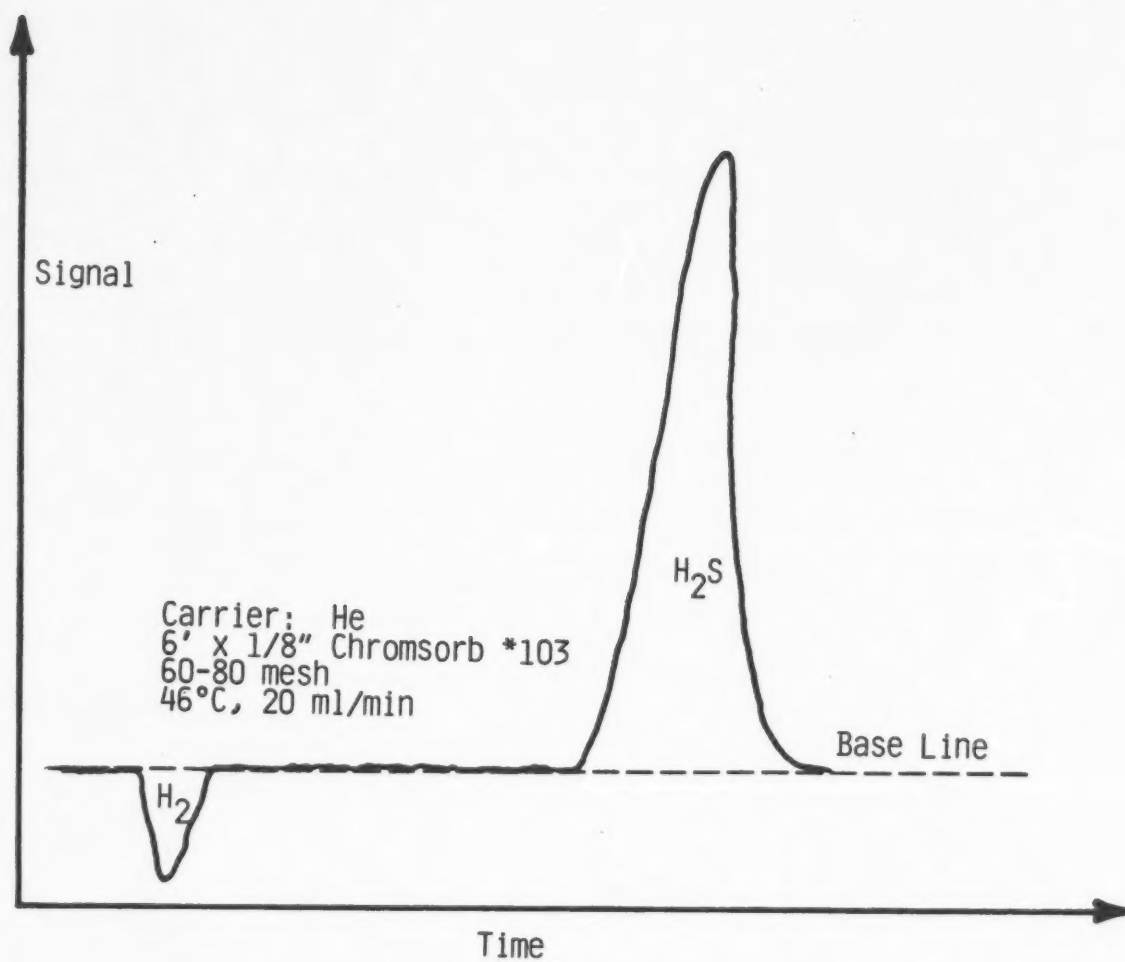


Figure 6.2 A typical output chromatogram

TABLE 6.4 MODES OF INTERPRETING THE GAS-SOLID REACTION DATA

Mode of Nucleation	Random Nucleation				Uniform Nucleation		
	Chemical Reaction Controls		Diffusion Controls		Chemical Reaction Controls		Diffusion Controls
	Unreacted surface	Nuclei peripheri	Unreacted surface	Nuclei peripheri	Unreacted surface	Nuclei peripheri	Unreacted surface
Location of Reaction							
Mode of Growth							

In each case, the shape of the growing nuclei can be assumed to be the same as that of the fully grown crystal or behave ideally as a crystal with a given shape or volume-to-surface ratio. Another problem that should be addressed relates to the timing of the nucleation. When random nucleation occurs, the new phase nucleates over a relatively long span of time. However, when a "uniform nucleation" occurs, all the nuclei are formed at approximately the same time. Therefore, they will grow and maintain more or less the same shape and size until they begin to coalesce. Microscopic studies of surfaces of many ionic crystals show uniform-sized crystals of the new phase, while growth of oxides on metallic surfaces appears to follow in many cases a random nucleation course. The main assumptions used in the following discussion are:

- 1) Nucleation of FeS on FeS₂ is uniform.
- 2) The newly formed FeS crystals are uniform in shape and size.
- 3) The rate of reaction is of the first order relative to the gas and the reaction is isothermal.
- 4) The nuclei are growing independently from each other.
- 5) The growing crystals do not coalesce.
- 6) The apparent rate of reaction is controlled by the rate of the chemical reaction and not the diffusion.

Before nucleation occurs, the surface reacts according to:

$$k_1 SC = \frac{dm}{dt} S \quad (6-7)$$

Since the surface area does not change much and because the thickness of the product layer is small, equation (6-7) can be integrated to:

$$m = k_1 Ct \quad (6-8)$$

or: $m = k_1 Ct =$

$$\delta_o = \frac{k_1 Ct_o}{\rho} = \frac{k_1 C}{\rho} i_o \theta \quad (6-9)$$

If the surface layer of thickness δ_o nucleates instantaneously, it will form n nuclei per unit area each with volume v :

$$v = \frac{m}{n\rho} \quad (6-10)$$

If each growing nuclei occupies initially area s , then

$$S_f = S - Sns = S(1-ns) \quad (6-11)$$

where S_f is the free surface area/unit surface area. The shape and rate of growth of the nuclei determine the magnitude of S_f . If the nuclei are rectangular with a boxy shape, then:

$$s = a^2 \quad (6-12)$$

and if they are cylindrical or hemispherical, then:

$$s = \pi r^2 \quad (6-13)$$

If the rate of growth is controlled by the rate of the chemical reaction, one may consider two cases: 1) reaction at the free surface area, denoted (FS); and 2) reaction at the interphase between the nuclei and the unreacted surface, denoted (PR).

6.5.1 Free Surface (FS) Models

For the FS model one may write:

$$S \frac{dm}{dt} = kCS_f = kSC(1-ns) \quad (6-14)$$

where s depends on the shape of the nuclei. For rectangular nuclei which grow only vertically, using equation (6-12),

$$m = \rho a^2 hn \quad (6-15)$$

and if the nuclei grow only horizontally:

$$\frac{dm}{dt} = kC(1 - \frac{m}{\rho h_0}) \quad (6-16)$$

and integration from m_0 to t_0 to m at t yields, for $h = h_0$:

$$-\rho h_0 \ln \frac{\rho h_0 - m}{\rho h_0 - m_0} = kC(t - t_0)$$

$$\frac{(\rho h_0 - m)}{(\rho h_0 - m_0)} = e^{-\frac{kC}{\rho h_0} (t - t_0)} \quad (6-17)$$

Assuming that nucleation occurred at t_0 to form crystals of height h_0 ,

$$Sh_0 na_0^2 = \delta_0 S \quad h_0 = \frac{\delta_0}{na_0^2} = h \quad (6-18)$$

If i pulses were injected each contacting the solid θ time, then:

$$t = i\theta \quad (6-19)$$

If A_i modes of H_2S were formed in the i^{th} pulse, then:

$$m = \frac{1}{S} \sum A_i \quad (6-20)$$

and equation (6-16) becomes:

$$\frac{\rho h_0 S - \sum_{i=1}^i A_i}{\rho h_0 S - \sum_{i=1}^0 A_i} = e^{-\theta \alpha (i - i_0)} \quad (6-21)$$

where

$$\alpha = \frac{kC}{\rho h_0} \quad (6-22)$$

This model holds until the growing nuclei begin to coalesce.

Similar analyses for hemispherical nuclei yield:

$$\frac{\beta k C t}{3} = m_0^{1/3} - m^{1/3} - \frac{1}{2\sqrt{\beta}} \ln \left[\frac{(1 + \beta m^{1/3})(1 - \beta m_0^{1/3})}{(1 + \beta m_0^{1/3})(1 - \beta m^{1/3})} \right] \quad (6-23)$$

where:

$$= \left(\frac{9}{4} n \right)^{1/3} \quad (6-24)$$

Note that if $\beta m_0^{1/3} \ll 1$,

$$\frac{1 - \beta m_0^{1/3}}{1 + \beta m_0^{1/3}} \approx 1 - 2 m_0^{1/3} \quad (6-25)$$

Therefore, equation (6-23) becomes:

$$\frac{\beta k C}{3} t = m_0^{1/3} - m^{1/3} - \frac{1}{2\sqrt{\beta}} n \frac{(1 - 2\beta m_0^{1/3})(1 + \beta m^{1/3})}{(1 - \beta m^{1/3})} \quad (6-26)$$

Again, one may substitute equations (6-19) and (6-20) in equation (6-23) or (6-26) to obtain the pulse dependence of the conversion.

Several other models may be devised; however, the *experimental results that were obtained for the system $\text{FeS}_2\text{-H}_2$ do not support the free-surface model. The main reason is that the free-surface approach predicts ever-decreasing rate of conversion, while it was observed that the rate of reaction first increases and then decreases.*

6.5.2 Perimeter Reaction Models (PR)

In the perimeter reaction model, the gas reacts on the perimeters of the nuclei or microcrystallites. This interphase line first increases as the nuclei grow and then decreases when the crystallites begin to coalesce. Therefore, such a model can account for the empirical observation that the rate of reaction first increases and then decreases.

For the fraction of time where the nuclei are growing independently and no coalescence occurs, one may write:

$$S \frac{dm}{dt} = k_2 S p \quad (6-26)$$

where p is the length of interphase contact, or perimeter, per unit surface area. Equation (6-25) can be integrated for different nuclei geometries and the results used to evaluate k_2 . Several examples are discussed below.

Example 1. Rectangular nuclei which are growing at a constant height h_0 , for which:

$$m = a^2 h_0 \rho n \quad (6-27)$$

and $p = 4an = 4n \cdot \left(\frac{m}{h_0 \rho n} \right)^{1/2}$

Therefore:

$$\frac{dm}{dt} = 4k_2 \left(\frac{mn}{h_0 \rho} \right)^{1/2} \quad (6-28)$$

$$m^{1/2} - m_0^{1/2} = 2k_2 \left(\frac{n}{\rho h_0} \right)^{1/2} (t - t_0) \quad (6-29)$$

Example 2. Rectangular boxes which grow uniformly:

$$m = a^3 \rho n \quad (6-30)$$

$$p = 4an = 4n \cdot \left(\frac{m}{\rho n} \right)^{1/3} \quad (6-31)$$

and

$$\frac{dm}{dt} = k_2 4n \left(\frac{m}{\rho n} \right)^{1/3} \quad (6-32)$$

$$\frac{3}{2} [m^{2/3} - m_0^{2/3}] = 4k_2 n \left(\frac{1}{\rho n} \right)^{1/3} (t - t_0) \quad (6-33)$$

$$m^{2/3} = m_0^{2/3} + \frac{8}{3} k_2 n \left(\frac{1}{\rho n} \right)^{1/3} (t - t_0) \quad (6-34)$$

or:

$$\left(\sum_{i=1}^i A_i \right)^{2/3} = \left(\sum_{i=1}^{i_0} A_i \right)^{2/3} + \frac{8}{3} k_2 n \left(\frac{S^2}{\rho n} \right)^{1/3} (i - i_0) \quad (6-35)$$

Figure 6.4 shows a plot of the $\left(\sum A_i \right)^{2/3}$ and $\left(\sum A_i \right)^{0.8}$ vs. i . The lines are close to being straight which supports the proposed model. The deviation from linearity increases around pulse #80 where the rate of reaction reaches a maximum. This point could correspond to the beginning of coalescence of nuclei. The plot of $m^{0.8}$ vs. i appears more linear than that of $m^{2/3}$ vs. i . It is believed that this is because not all the nuclei form simultaneously as assumed and because the nuclei do interact with each other and do not grow independently as assumed. Nonetheless, the agreement of the data with the model is excellent.

At the point where the rate of reaction reaches a maximum (i.e., pulse 55 of the 375°C run), the cumulative amount of FeS (or H₂S) formed is about $6.8303 \cdot 10^{-6}$ moles/gm FeS₂. If the specific surface area of the sample is $0.0057 - 0.01$ m²/gm, then for particles of an average size of 104 microns, coalescence of nuclei begins when about $1.19 \cdot 10^{-7}$

Log x_1 vs. t

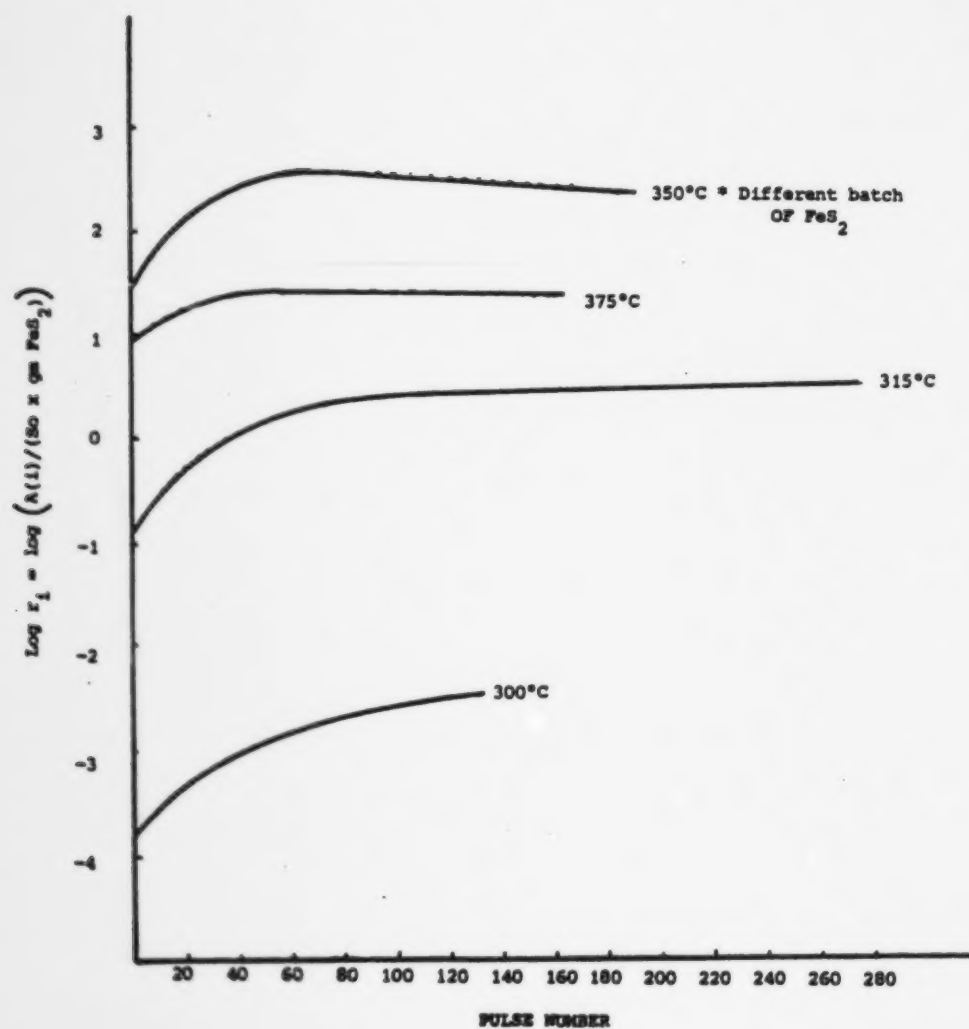


Figure 6.3 Kinetics of pyrite reduction

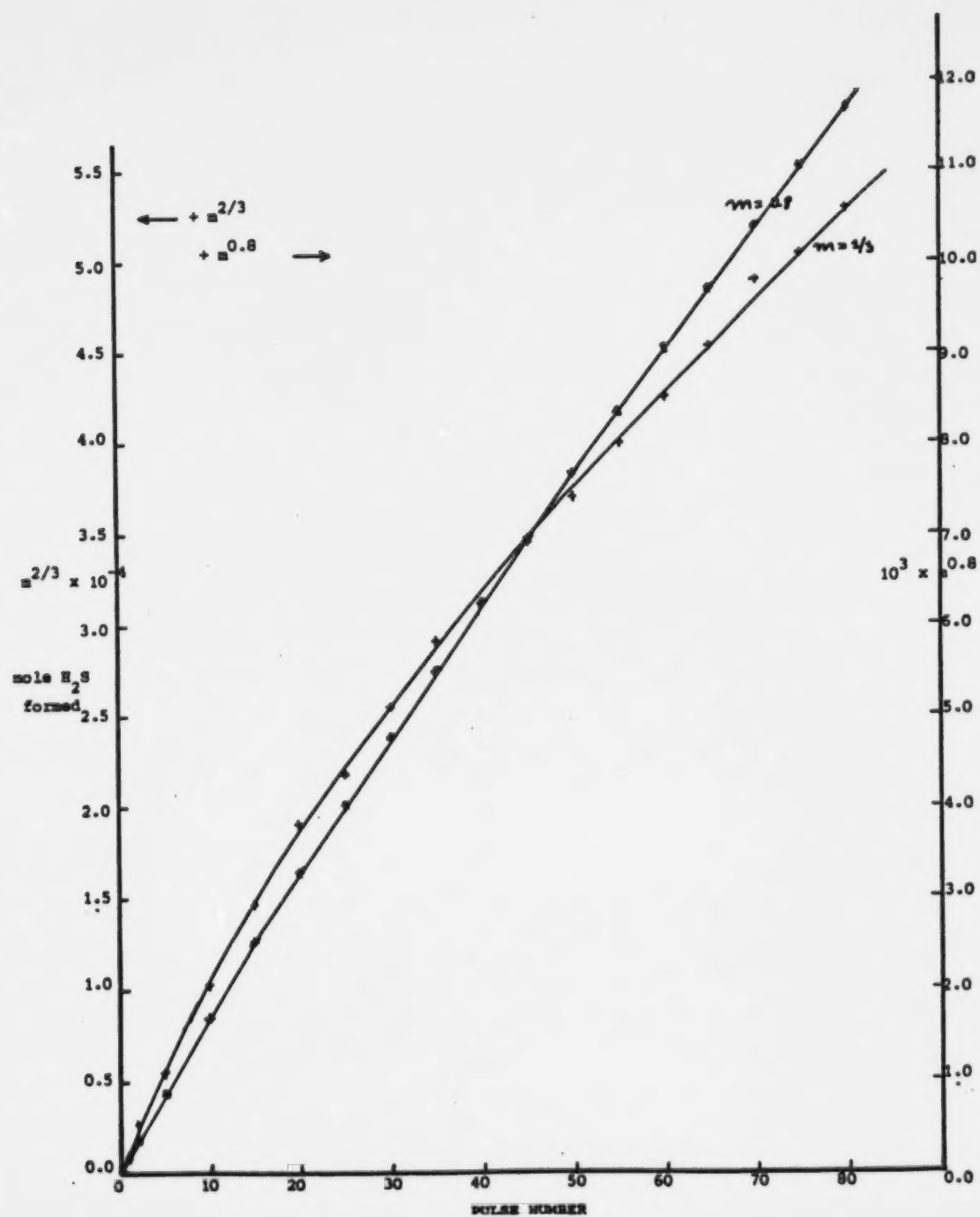


Figure 6.4 Kinetics of pyrite reduction before coalescence

moles/cm² are formed on the surface. The thickness of this layer of product, had it been uniform, would have been about $2.05 \cdot 10^{-6}$ cm or 0.02 microns (205 Å). This corresponds to approximately 15-75 layers of molecules on the surface. Thus, coalescence of the nuclei occurs rather rapidly in the case of the reduction of FeS₂ by H₂.

Note that other nuclei geometries and growth mode can be tried. Thus, if the nuclei were hemispherical, the rate equation corresponding to equations (6-34) and (6-35) would be:

$$m^{2/3} = m_0^{2/3} + k_2 \theta \left(\frac{32\pi^2}{gn} \right)^{1/3} (t - t_0) \quad (6-36)$$

and:

$$\left(\sum_{i=1}^i A_i \right)^{2/3} = \left(\sum_{i=1}^{i_0} A_i \right)^{2/3} + k_2 \theta \frac{S^2 32\pi^2}{gn} (i - i_0) \quad (6-37)$$

Note further that the hemispherical rate law, equation (6-37), also predicts a power dependence of 2/3 rather than the observed 0.8.

The slopes, the intercepts and the correlation coefficients of the $n = 2/3$ and $n = 0.8$ lines are summarized in Table 6.5. The intercept at $i = 0$ in the case of $n = 0.8$ is an order of magnitude smaller than for $n = 2/3$. Note that even though very small pulses are used, it is difficult to identify when nucleation occurred. Apparently, nucleation of FeS occurs on the FeS₂ almost instantaneously.

6.6 CONCLUSIONS

The initial period of the reaction of FeS₂ with H₂ was studied in the temperature range of 300-375°C. A pulsed differential reactor was used which allowed to follow the very small surface conversion in isothermal conditions. The nucleation of the new phase of FeS on the FeS₂ surface appears to be instantaneous and the growth of the FeS crystals proceeds initially by the reaction of the hydrogen on the perimeter of the nuclei. The FeS crystallites grow and then coalesce; however, as long as they grow the perimeter length/surface area increases and the apparent rate of reaction increases. However, once the crystallites

coalesce, the specific perimeter begins to decrease and so does the apparent rate of reaction.

TABLE 6.5 PARAMETERS OF NUCLEIC GROWTH LINE, 375°C

n	Slope	Intercept	Correlation Coefficient
2/3	$6.38638 \cdot 10^{-6}$	$4.16465 \cdot 10^{-5}$	0.99532
0.8	$1.457 \cdot 10^{-6}$	$2.64428 \cdot 10^{-6}$	0.99939

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6.8 NOMENCLATURE

- k_1 - reaction rate constant, cm/sec (before nucleation)
 k - reaction rate constant, cm/sec (after nucleation)
 S - specific surface area, cm^2/gm
 C - gas concentration, moles/ cm^3
 m - moles products formed per unit surface area, moles/ cm^2
 t - time sec.
 i_0 - no. of pulses before nucleation occurs
 n - no. of nuclei/unit area, $\#/\text{cm}^2$
 v - volume of surface nuclei, cm^3
 s - surface area occupied by a growing product crystal
 s_0 - initial surface area of a nuclei
 Sp - free specific surface area, cm^2/gm
 a - side length of a nuclei
 r - radius of a nuclei
 h - height of a crystal of products
 A_i - moles of H_2S formed in the i -th pulse
 α - equivalent reaction rate constant, cm/sec - rectangular geometry
 β - equivalent reaction rate constant, cm/sec - rectangular geometry
 ρ - product density, mole/ cm^3
 δ - critical thickness of product layer before nucleation occurs, cm
 θ - average residence time of the gas pulse near the surface

CHAPTER 7

COAL STRUCTURE AND ITS RELATION TO THE ADHERENCE OF MINERALS TO COAL SURFACES

The structure of the coal, in particular the sulfur and oxygen functional groups in it, can have a dramatic effect on the amount of sulfur retained in the ash. The main structural features which can influence sulfur retention in coal ash are summarized in Table 7.1.

Table 7.1 shows that the nature of the sulfur functional groups influences the temperature at which H_2S will evolve from the organic matrix. The oxygen functional groups influence mainly the quantity of calcium which can be ion exchanged with the coal and the strength of adherence of the mineral matter particles.

In this chapter, the following subjects will be covered:

- 1) Results on the inorganic and organic forms of sulfur in 22 coals (this work was partially sponsored by DOE).
- 2) Results and the methodology used to determine oxygen functionalities in three coals.
- 3) Adsorption and desorption isotherms of oxygen and CO_2 on three coals before and after removal of the calcium by HCl extraction.
- 4) Measurements of the strength of surface forces of three coals using the adsorption-desorption data and chromatographic methods, and
- 5) The effect of neutralizing the surface phenols on the adherence of mineral particles to the surface.

7.1 OBJECTIVES

The objective of this task was to generate data on the structure of coal so that it may be possible to derive a general model which relates the fundamental properties of the coal and its behavior during combustion.

TABLE 7.1 STRUCTURAL PARAMETERS WHICH INFLUENCE
SULFUR RETENTION IN COAL ASH

Feature	Influence
1. Concentration of Thiols, RSH	Thiols decompose readily and release H_2S in early stages of the combustion, ~ 200 - $300^\circ C$.
2. Sulfides, RSR'	Sulfidic groups decompose in the temperature range of 250 - $400^\circ C$ and release H_2S .
3. Thiophenes, $C_4H_{4-n}SR_n$	Usually volatilize with the coal volatiles around 380 - $550^\circ C$.
4. Carboxyls, $RCOOH$	Present mainly in low-ranked coal. Capable of ion-exchanging calcium and thus maintaining calcium in a finely divided form in the coal. $RCOOH$ decomposes in the temperature range of 300 - $500^\circ C$.
5. Hydroxyls and phenols, OH	Present more in bituminous and in high ranked coals. Act like carboxyls except that they are less acidic and more stable.
6. Carboxyls and ethers	Are polar groups which increase the density of polar surface groups and thus the adherence of minerals to the surface. Carboxyls and ethers are less abundant in coals than phenols.

7.2 ORGANIC SULFUR FUNCTIONALITIES

This work was begun under DOE sponsorship (Attar and Dupuis, 1978, 1981; Attar, 1982, and in print, Attar, 1982). Since the methodology was published as well as some of the results, only the tables of the complete set of results will be presented here. Table 7.2 gives the ASTM D2492 sulfur analysis of 19 coals and Table 7.3 gives the distribution of sulfur functionalities in these coals.

The data show that a great variability exists in the sulfur forms in different coals and no clear correlation with the rank or with other parameters can be observed. From the LIMB viewpoint, it may be noted

TABLE 7.2 SULFUR FORMS IN DIFFERENT COALS

Coal	S _{total} %	S _{pyritic} %	S _{sulfate} %	S _{organic} %
1. N.C. peat	0.25	0.002	0.02	0.23
2. Beulah lignite (N.D.)	0.46	--	--	0.46
3. Texas lignite (Wilcox formation)	1.20	0.4	--	0.80
4. Texas lignite (Milam Co.)	0.95	0.323	0.195	0.90
5. Wyodak, Subbitumin- ous (WY)	0.90	--	--	0.90
6. N.M., Subbituminous	1.24	0.45	0.15	0.64
7. Amax, Subbituminous	0.04	--	--	0.04
8. Ill. #6, Montrey	4.50	1.23	0.06	3.2
9. Pittsburgh #8, Ireland				
10. Kentucky #9	4.23	2.12	0.21	1.90
11. Kentucky #9 + 14	6.6	5.05	0.135	1.43
12. Lower Kittaning (WVA)	2.20	1.48	0.12	0.60
13. Pittsburgh Seam, Westland (PA)	2.60	1.05	0.07	1.48
14. Colberg Seam (WVA)	2.29	1.39	0.02	0.88
15. Pittsburgh #8, Jefferson Co. (OH)	1.70	1.23	0.01	0.46
16. Lower Freeport (WVA)	2.32	1.17	0.28	0.87
17. Bevier (Missouri)	3.40	0.90	0.03	2.47
18. W. Kentucky (Island Creek)	3.54	1.97	0.04	1.53
19. Upper Stockton (WVA)	1.01	0.06	0.00	0.95

TABLE 7.3 SULFUR FUNCTIONALITIES IN DIFFERENT COALS (MOLE 10^5 /GM)

Coal	Wt. % Organic S	10^5 x moles sulfur/gm coal					
		Aliphatic Thiols	Aromatic Thiols	Aliphatic Sulfides	Aryl Sulfides	Simple Thiophenes	Complex Thiophenes
1. N.C. peat	0.23	0.05	--	0.1	--	0.08**	
2. Beulah lignite (N.D.)	0.46	--	0.52	2.0	16.9	--	10.1
3. Texas lignite (Wilcox formation)	0.80	1.63	5.25	4.25	6.00	7.88*	--
4. Texas lignite (Milam Co.)	0.90	--	--	4.78	2.70	4.58	16.06
5. Wyodak, Subbitumin- ous (WY)	1.30	--	--	4.33	0.53	25.88*	--
6. N.M., Subbituminous	0.64	0.20*	--	0.30	--	0.14**	--
7. Amax, Subbituminous	0.50	1.72	--	1.84	3.05	3.50	5.51
8. Ill. #6, Montrey	3.2	7.00	15.00	18.00	2.00	58.00*	--
9. Pitts. #8, Ireland mine							
10. Kentucky #9	1.90	6.14	0.36	1.39	6.25	2.34	42.90
11. Kentucky #9 + 14							
12. Lower Kittanning (WVA)	0.60	1.87	4.69	4.69	1.59	4.03*	--

TABLE 7.3 (CONTINUED)

Coal	Wt. % Organic S	10 ⁵ x moles sulfur/gm coal					
		Aliphatic Thiols	Aromatic Thiols	Aliphatic Sulfides	Aryl Sulfides	Simple Thiophenes	Complex Thiophenes
13. Pittsburgh Seam, Westland (PA)	1.48	13.88	13.88	11.79	--	6.71*	--
14. Colberg Seam (WVA)	2.29			39.3	63.3	215	37.5
15. Pittsburgh #8, Jefferson Co. (OH)	1.85	5.66	1.95	3.49	1.39	1.32	44.00
16. Lower Freeport (WVA)	0.87	7.44	3.62	1.41	--	14.72*	--
17. Bevier (Missouri)	2.47	11.00	3.53	6.22	9.53	4.78	42.12
18. W. Kentucky (Island Creek)	1.53	6.53	5.94	6.28	3.38	2.12	23.56
19. Upper Stockton (WVA)	1.01	3.6	--	13.7	7.2	3.63	34.2

*Includes complex thiophenes.

that most of the organic sulfur in low-ranked coals is thiophenic, while 15-45% of the organic sulfur in high sulfur coals is thiolic and sulfidic, i.e., is present in forms which may release H_2S in the early stages of the combustion.

7.3 CARBOXYLS, PHENOLS AND HYDROXYLS IN THREE COALS

The total concentration of carboxyls, phenols and hydroxyls in three coals was determined using the method of Blom (1960) as modified by Cronaur et al. (1979). The modified method used in our laboratory is described in the Appendix to this chapter. Table 7.4 gives the data obtained. As expected, more carboxyls are present in the lower ranked coals than in the higher ranked coals. The quality of the data is as good and often much better than that reported in the literature.

From the LIMB point of view, one can see that even lignites, which have more carboxyls and phenols than other coals, do not have sufficient concentration of ion-exchangeable groups to tie enough calcium to stoichiometrically bind all their sulfur.

TABLE 7.4 IONIC SITES IN DIFFERENT COALS

Sample	Carboxyls meq/gm	Phenols meq/gm	Alcoholic meq/gm
1. Texas lignite	1.234	1.267	NO
Wilcox formation	1.230	1.223	NO
2. New Mexico	0.280	1.774	0.097
Subbituminous	0.282	1.704	0.1205
3. Ohio high-sulfur	0.215	1.320	0.146
	0.261	0.955	0.238

7.4 SURFACE VAN DER WAALS FORCES BY O_2 AND CO_2 ADSORPTION

The system described in Chapter 5 was used to measure adsorption and desorption isotherms of oxygen (O_2) and of carbon dioxide (CO_2).

of run-of-mine-coal and of HCl-treated coal at 0, 23, 64, 80 and 110°C, using a special cell design which allowed keeping the sample isothermal by maintaining it in a solvent at its reflux temperature. Figure 7.1 is a schematic diagram of the reflux cell. Table 7.5 lists the adsorption-desorption isotherms measured. Not all the experiments planned were already conducted, but the data show the main trends.

TABLE 7.5 ADSORPTION-DESORPTION ISOTHERM ALREADY MEASURED

Coal	Temp. °C	Adsorbent
1. Texas lignite, Wilcox formation	0, 25, 80.2, 110	O ₂
2. As #1 but HCl-treated*	0, 25, 80.2, 110	O ₂
3. As #1	0, 25, 80.2	CO ₂
4. High sulfur bituminous coal, Ohio	0, 25, 80.2	O ₂
5. As #4 HCl-treated*	0, 25, 80.2	O ₂
6. New Mexico subbituminous	0 ⁺ , 25 ⁺ , 80.2, 110	O ₂
7. As #6 HCl-treated*	0 ⁺ , 25 ⁺ , 80.2, 110	O ₂

*Leached with 1:1 HCl for 30 min, then with water, dried and stored under N₂.

⁺No adsorption was detected.

As expected, the lower ranked coals, which have more polar groups, adsorb more polarizable gases like CO₂ and O₂. This is consistent with the prevailing experience that it is more difficult to demineralize lower ranked coals, since the mineral particles adhere to the same polarizable groups on the coal surface.

Figures 7.2 to 7.8 are the adsorption isotherms obtained. Note that the shape of the 0 and 25°C oxygen isotherms follow classical patterns while the 80 and in particular the 110°C isotherms show an increase in the amount of O₂ adsorbed and certain irreversibility. The oxygen

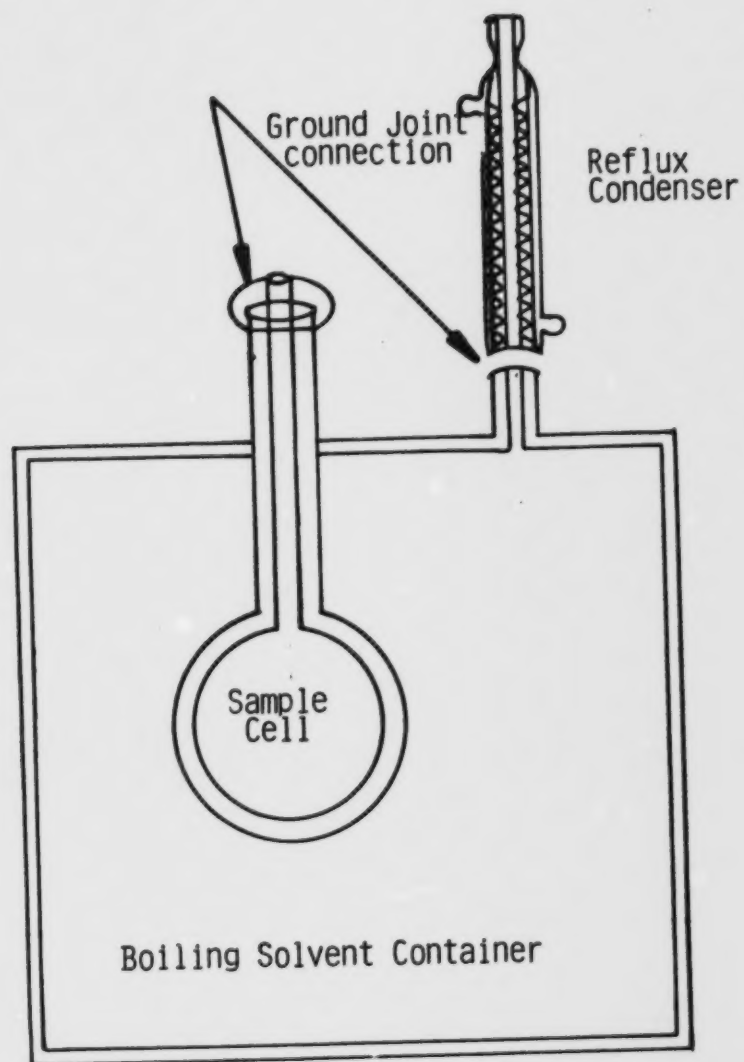


Figure 7.1 Reflux isothermal adsorption cell

TEXAS LIGNITE UNTREATED O_2 ADSORPTION
GRAPH I

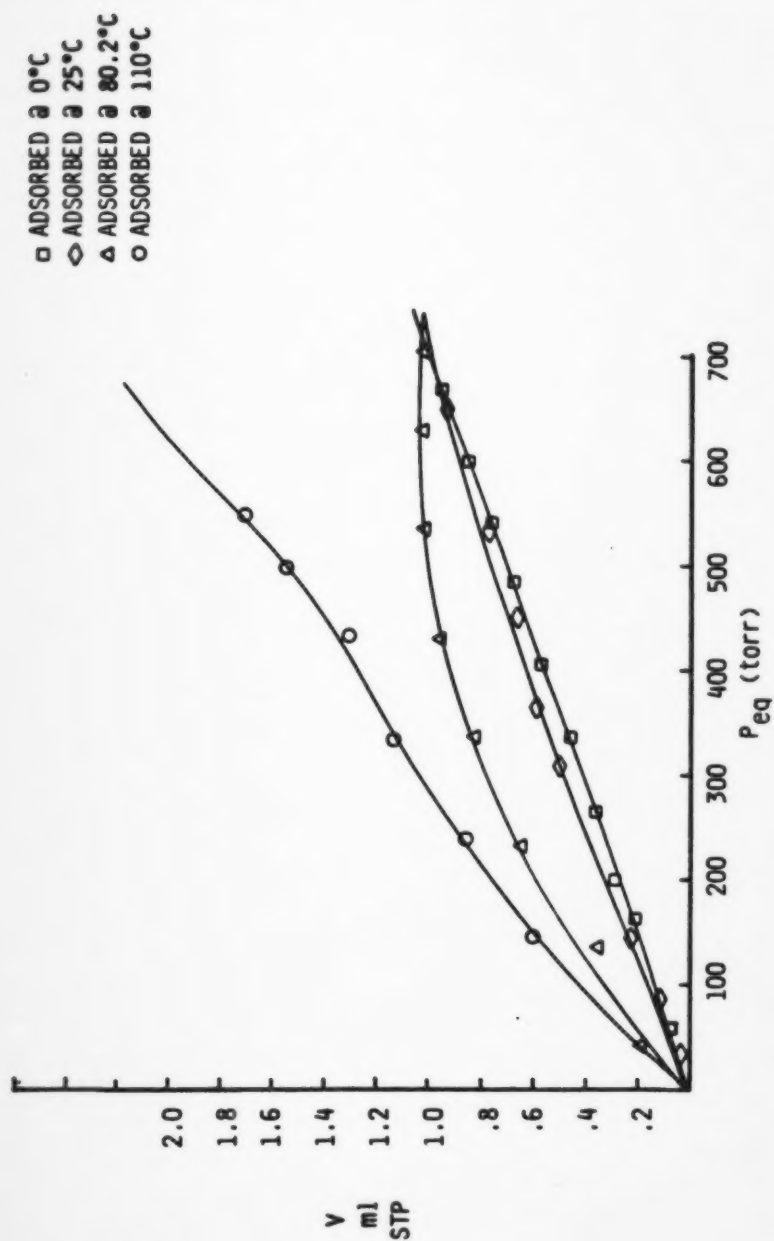


Figure 7.2 Adsorption isotherms for O_2 on Texas lignite surface at 0, 25, 80.2 and 110°C

TREATED TEXAS LIGNITE O₂ ADSORPTION
GRAPH II

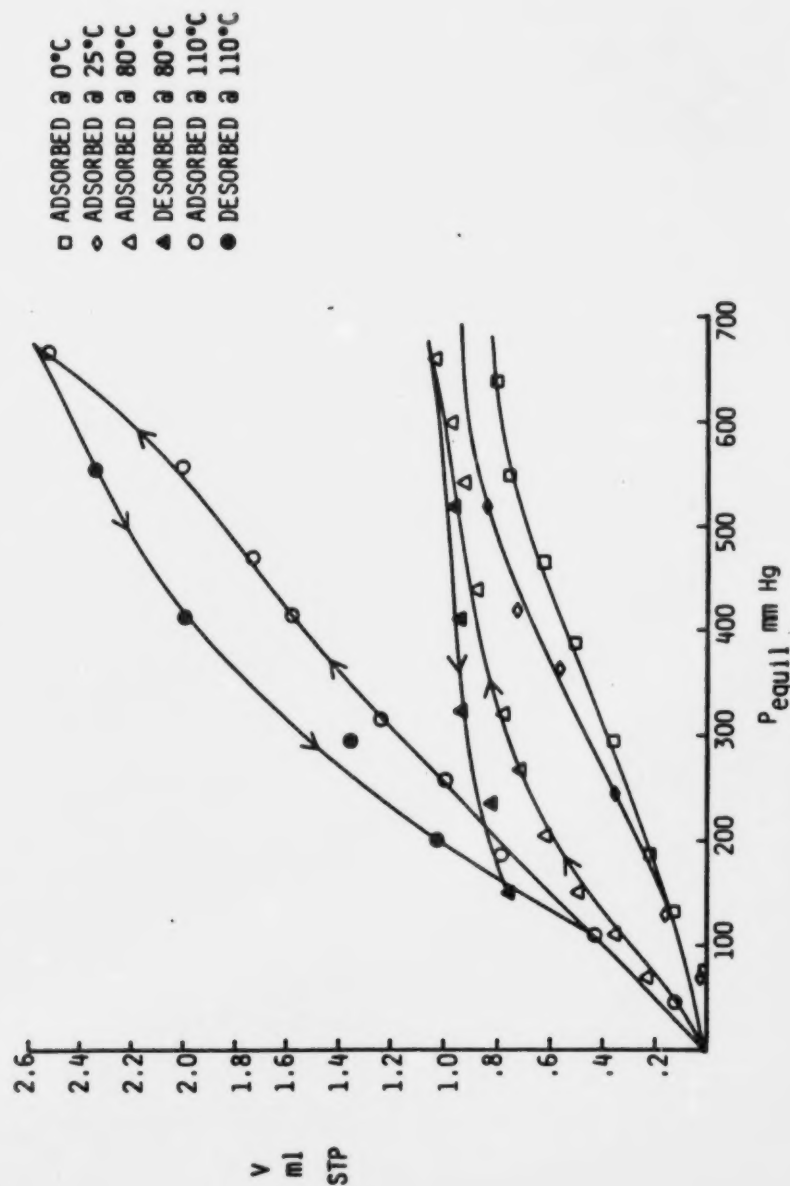


Figure 7.3 Adsorption isotherms for O₂ on HCl-treated Texas lignite surface at 0, 25, 80.2 and 110°C

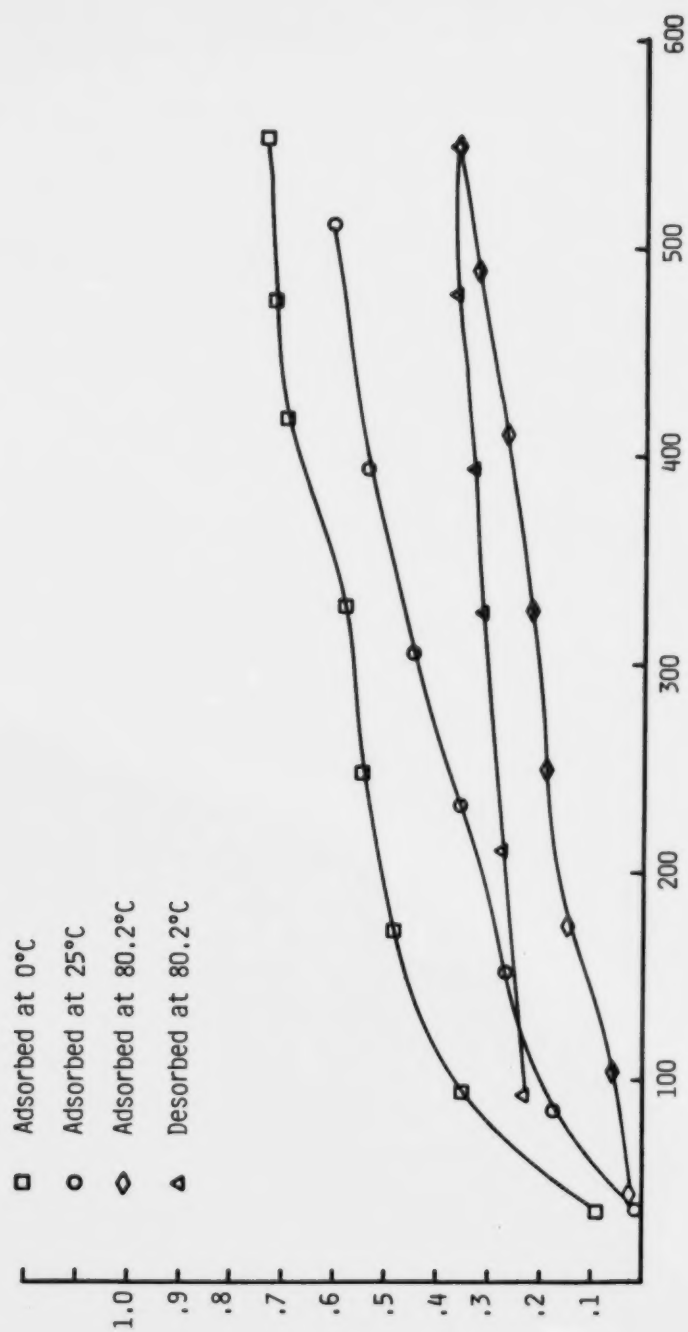


Figure 7.4 Untreated Texas lignite with CO_2 as adsorbate

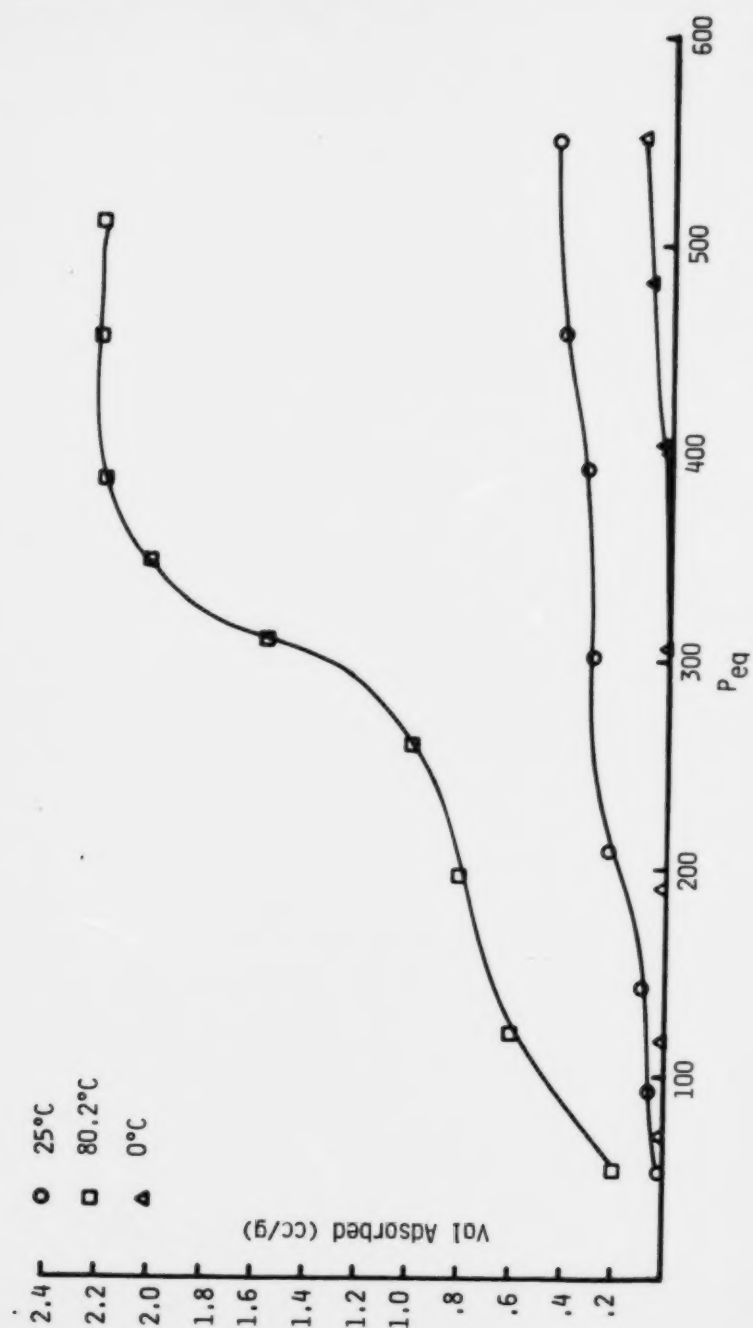


Figure 7.5 Untreated Ohio high sulfur



Figure 7.6 Treated Ohio high sulfur

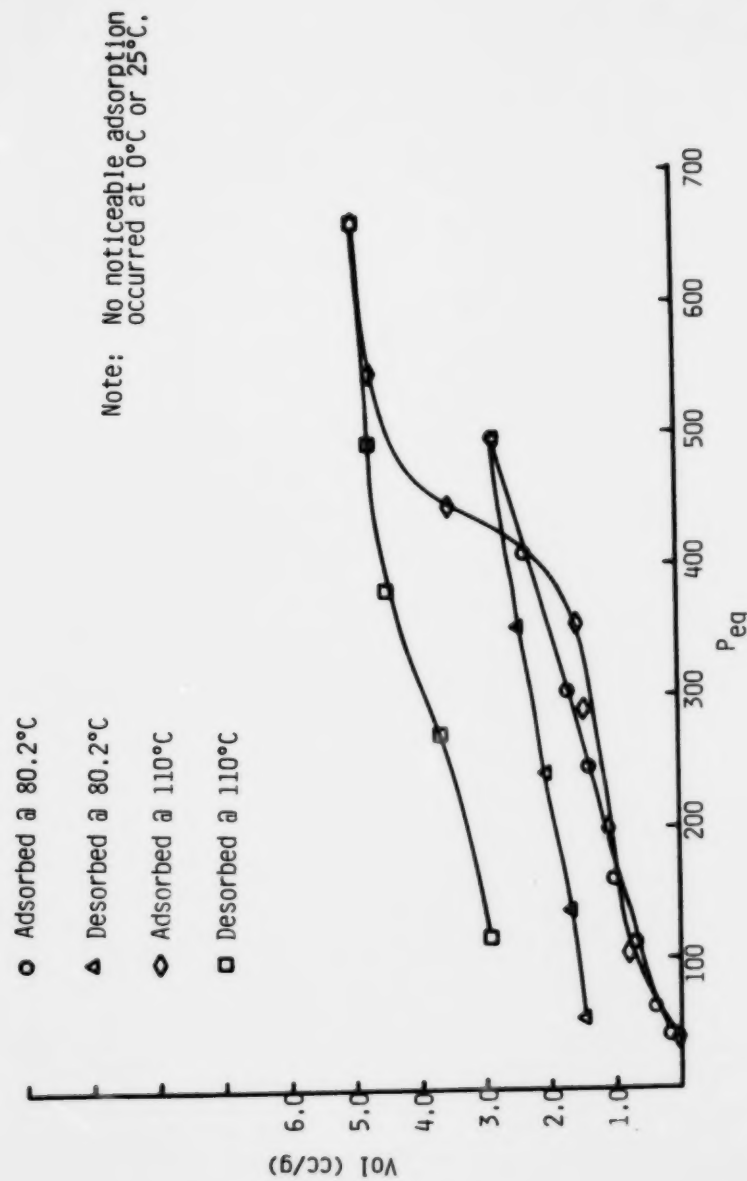


Figure 7.7 Untreated New Mexico subbituminous O_2 adsorbate

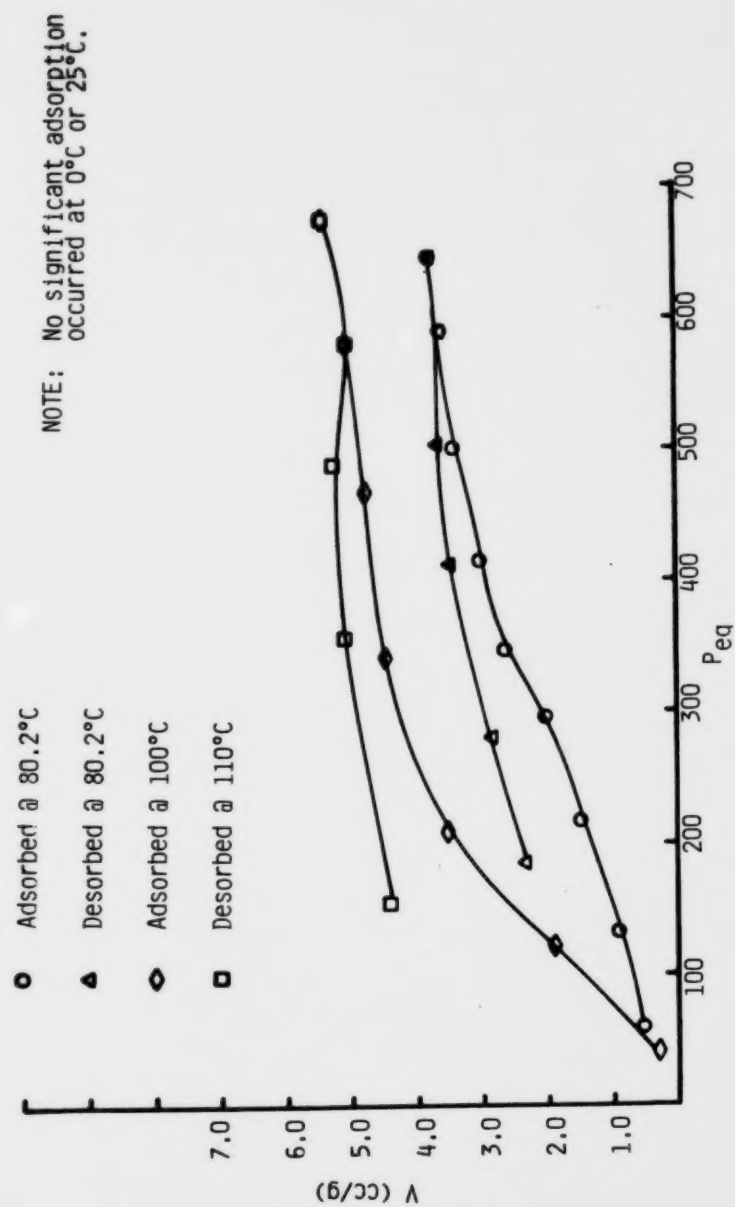


Figure 7.8 Treated New Mexico subbituminous O_2 adsorbate

oxidizes the coal and increases the surface polarity by increasing the concentration of polar groups on it. Therefore, CO_2 should be preferred as a gas for probing the surface since it does not react with the coal below 150°C and at about 1 atm.

HCl extraction of coals removes the calcium carbonates and ion-exchanged metals and appears to increase the surface area of coal. The quantities of O_2 adsorbed increase and equilibrium is reached faster, which indicates that the surface is more accessible to the gas.

7.5 STRENGTH OF SURFACE FORCES

Two methods were used to evaluate the strength of the surface forces: (1) comparison of the isosteric volume of adsorption at different temperatures (IVAT), and (2) chromatographic peak illution at different temperatures (CPIT). The IVAT method measures the average equilibrium enthalpy of adsorption while the CPIT method is more sensitive to the enthalpy of adsorption to functionalities closer to the coal particle surface.

7.5.1 IVAT Results

The enthalpy of adsorption is obtained from the slope of the curve obtained when the logarithm of the equilibrium adsorption volume at constant relative coverage, $\theta = P/P_s$, is plotted vs. $1/T$. Figures 7.9 and 7.10 show the curves obtained for rom and HCl-treated Texas lignites at two different coverages, using O_2 and 7.11 gives it for CO_2 . The value of ΔH calculated by multiplying the slope by $-R$ appears to be independent from the coverage. However, the value of ΔH for the HCl-treated lignite is somewhat larger than that obtained for the rom lignite, i.e., 4.5 vs. 3.9 kcal/mole.

7.5.2 CPIT Results

The enthalpy of adsorption is obtained from the slope of the curve of $\log(t_i - t_0)$ vs. $1/T_i$, where t_i is the residence time of a CO_2 pulse at temperature T_i and t_0 is the nonadsorbing gas residence time. The

UNTREATED TEXAS LIGNITE USING O₂ ADSORBATE

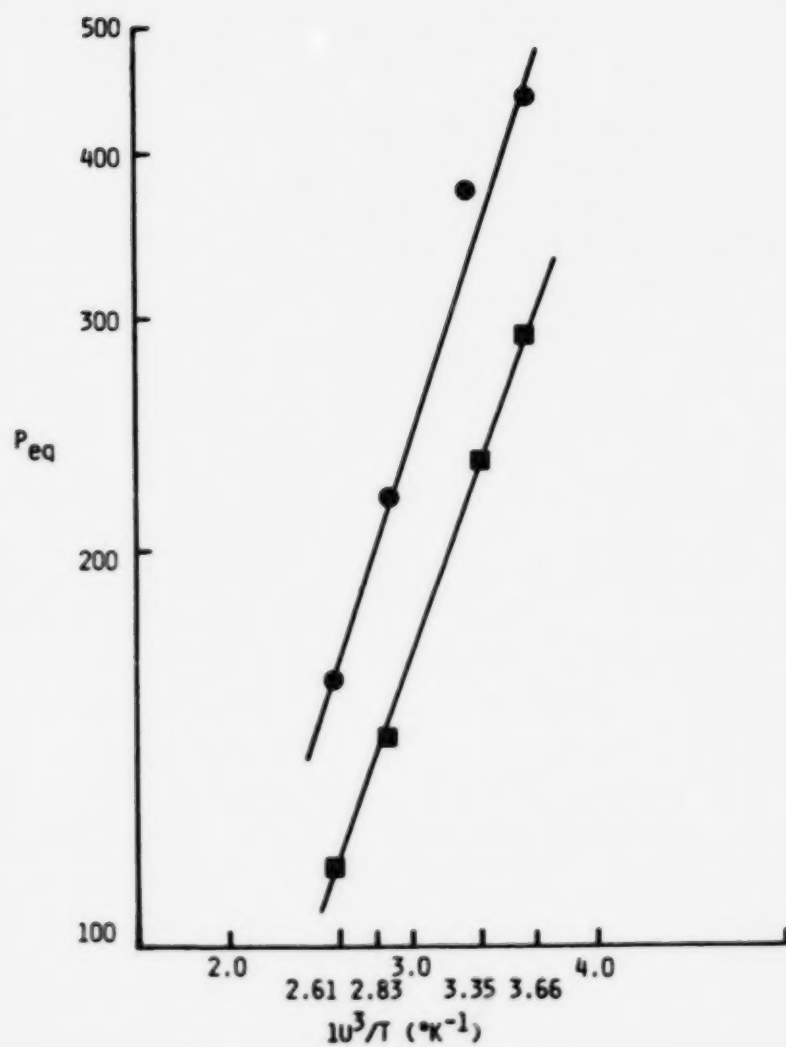


Figure 7.9 Isosteric adsorption pressures of O₂ on ROM lignite vs. 1/T

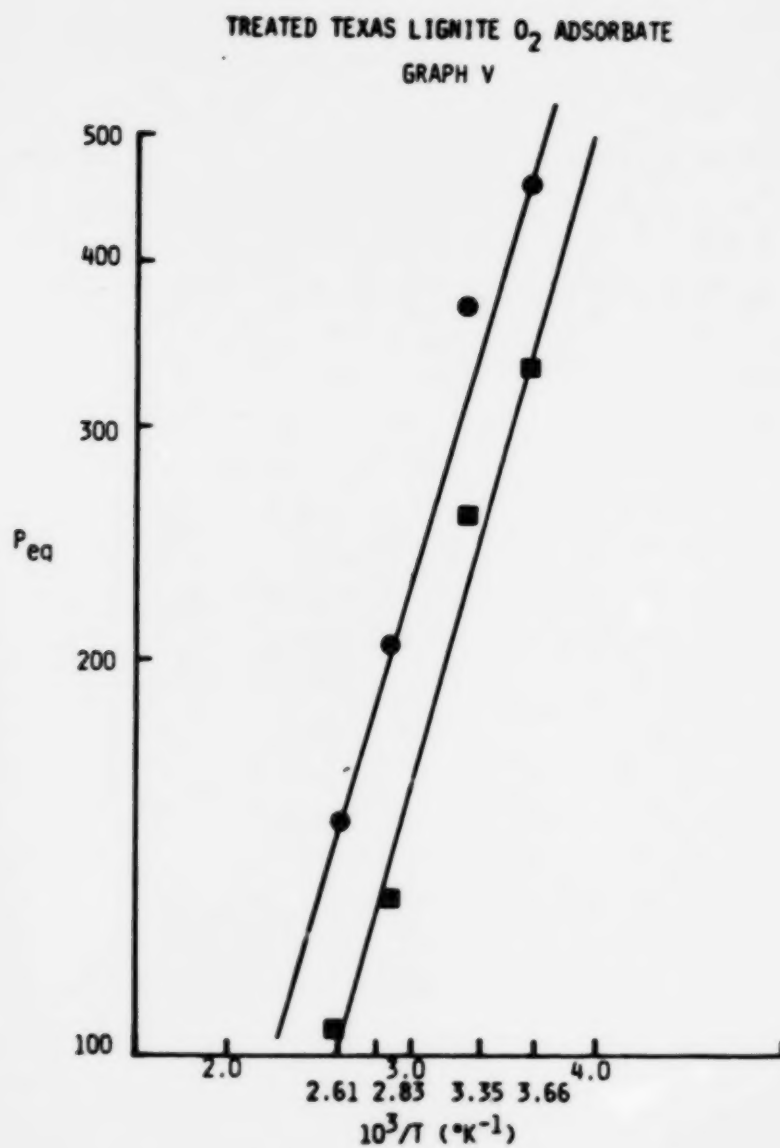


Figure 7.10 Isosteric adsorption pressures of O₂ on HCl-treated lignite vs. 1/T

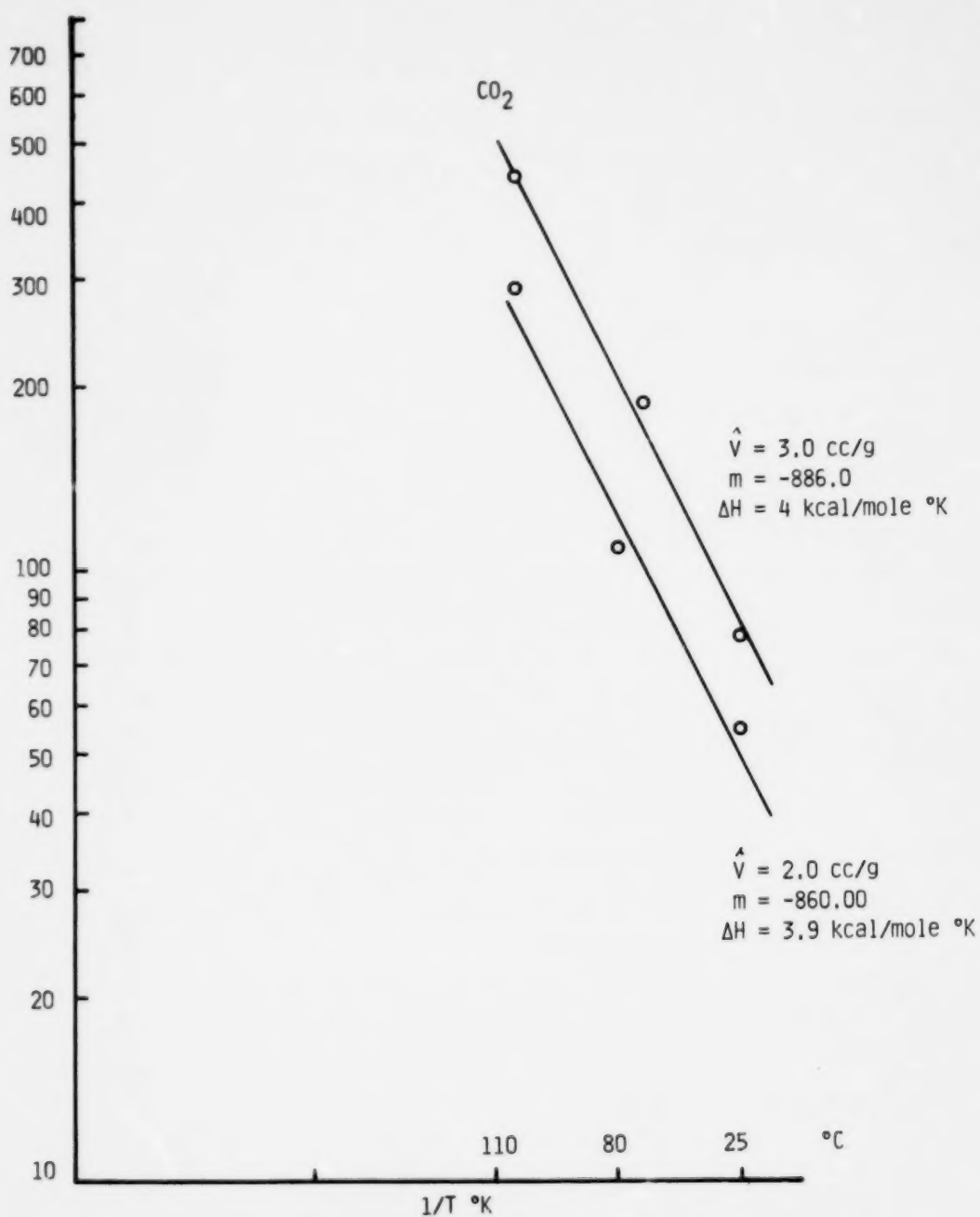
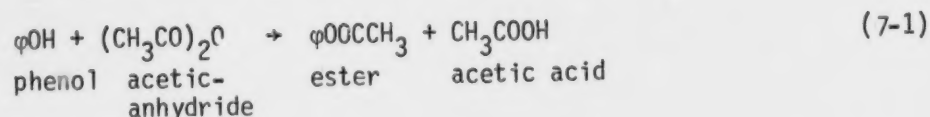


Figure 7.11 Isosteric heat of adsorption

value of the slope is multiplied by $-R$ to obtain ΔH . Figure 7.12 shows a typical curve obtained from Texas lignite. The calculated ΔH is about 7.1 kcal/mole which is significantly larger than obtained by the equilibrium method. This is not untypical since coal external surfaces are often oxidized and therefore are more polar than the coal bulk; the CPIT method will give a larger value for ΔH than the IVAT Method which gives a volume-average value.

7.6 SURFACE FUNCTIONS AND MINERALS ADHERENCE

Since the surface oxygen functions are believed to attract particles of the mineral matter and help them adhere to the surface, it was desired to determine whether neutralizing some of these forces will allow easier separation of the coal minerals. Since most of the polar groups on surfaces of bituminous coals are believed to be phenols, esterification was selected as the method of depolarizing the surface, i.e.:



The esteric group is much less polar than the phenolic groups and is incapable of ion-exchanging calcium.

Samples of Illinois #6 coal of different particle sizes were prepared and divided to two fractions: one was separated to a float and a sink using chloroform as a medium ($\rho = 1.45$) and the other was esterified with 20% $(\text{CH}_3\text{COO})_2\text{O}$ in chloroform for 1 hr at room temperature and then separated to a float and a sink. The sulfur and ash contents of each fraction were determined by standard methods and the data are plotted in Figure 7.13. Note that the scattering is large at the small particle sizes region. This is due to the poor separation technique which was used then. (Now we have a much better one.)

The data show that esterification of the surface, which reduces its polarity, allows to separate most of the minerals and to produce coal with a mineral level comparable to the inherent minerals level.

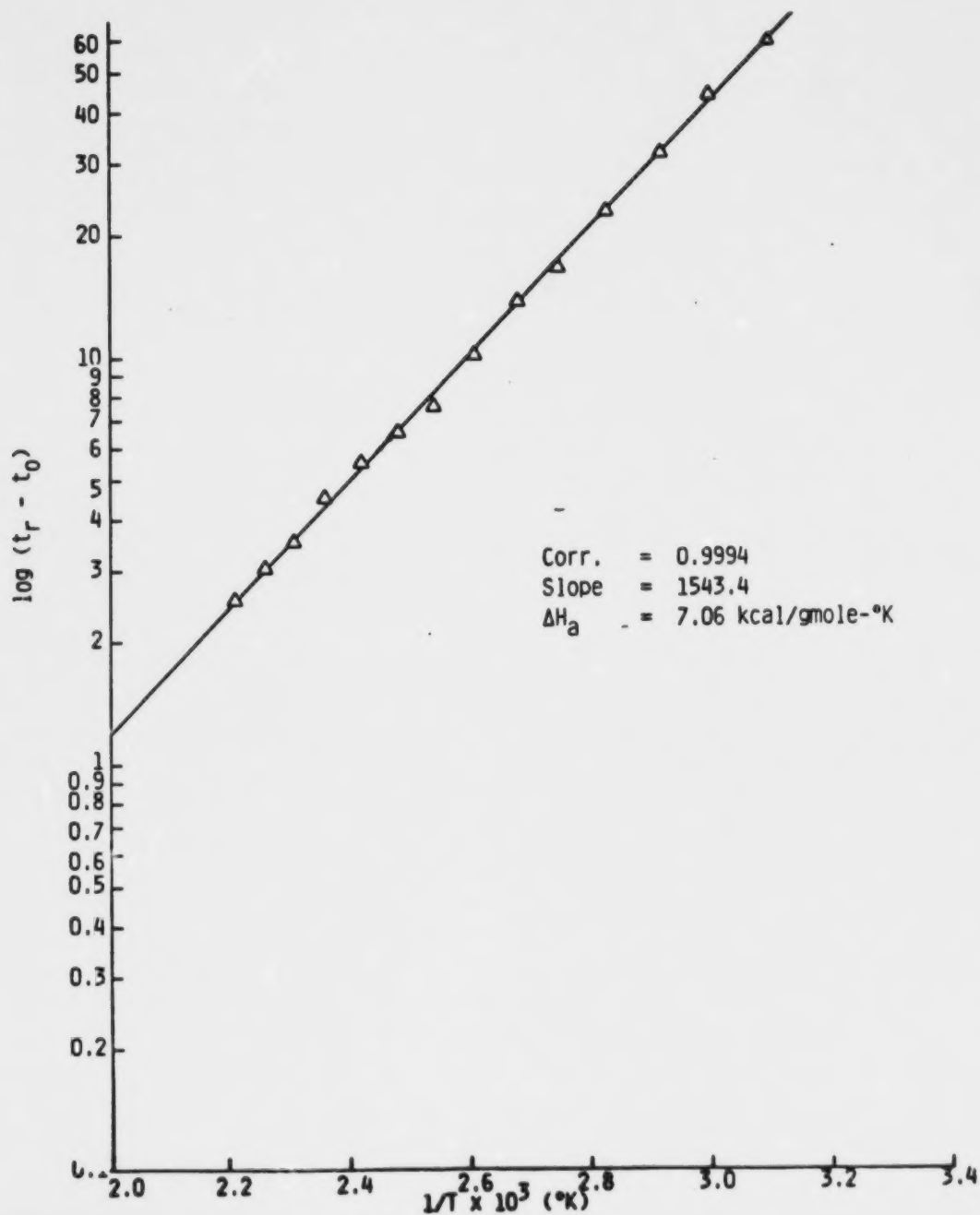


Figure 7.12 Log of net retention time of CO_2 vs. $1/T$, ROM Texas lignite (Wilcox formation)

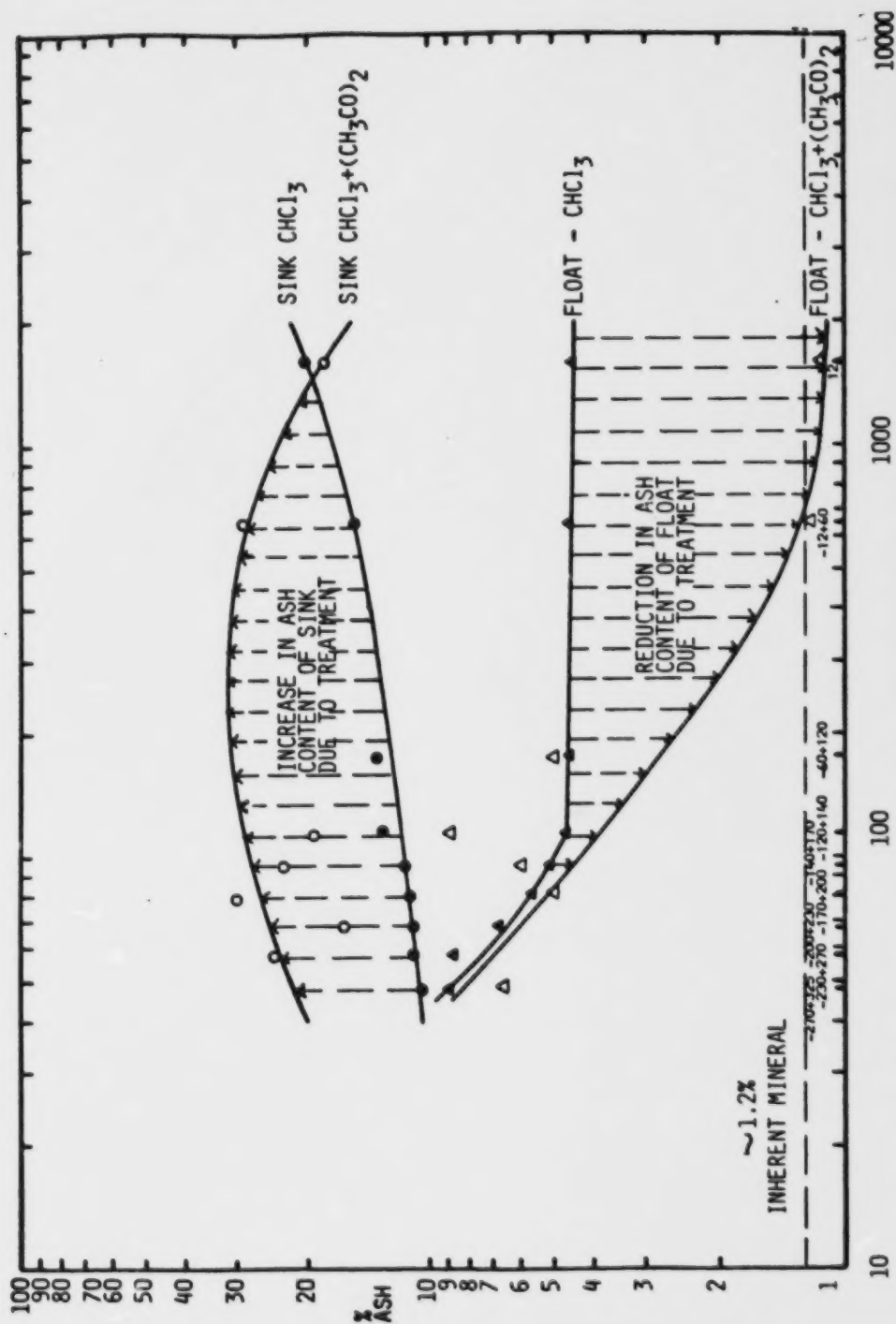


Figure 7.13 Ash contents of float and sink chloroform density fractions of Ill. #6 size-fractions with and without acetylation

Note that the quality of the separation deteriorates when small particles are considered. It is also believed that a poor separation will be obtained when very large coal particles will be treated.

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7.8 APPENDIX

7.8.1 Experimental Procedure for the Determination of Oxygen Functional Groups in Coal

Preparation of Coal Samples. Coal samples must be pulverized to ensure that all the functional groups are exposed, allowing the various reagents to reach these groups. Care must be taken not to grind the coal to fine because there is the possibility of these exceedingly fine particles retaining a static charge and hence making them difficult to wet. As specified by Blom et al., coal with a particle size less than 200 mesh was used.

HCl Pretreatment. Coal samples were treated with 1 N HCl, filtered, dried in a nitrogen atmosphere, and then stored in nitrogen in a procedure developed by Blom et al.¹ Pretreatment with HCl ensures that no salts are present and that all the oxygen functional groups are in a free state.

¹Blom, L. et al., Fuel, 36, 135 (1957).

Determination of Oxygen Functional Groups. Oxygen function groups were measured in the following coals: Texas lignite, New Mexico sub-bituminous, and Ohio high-sulfur. Total OH functional groups, alcoholic OH groups and carboxylic groups (COOH) measurements were made for each coal. Methods for determining these functional groups were those developed by Blom et al.

7.8.2 Experimental Procedure to Determine the Heats of Adsorption of Carbon Dioxide, Oxygen, and Dimethyl ether on Coal

Adsorbents. The three coals used in this work were Texas lignite, New Mexico subbituminous and Ohio high-sulfur. Two samples of each particular coal were used, with one sample of each having undergone the HCl pretreatment developed by Blom et al. HCl pretreatment insures that no salts are present and that all the oxygen functional groups are in a free state.

Experimental Apparatus. A Varian 3700 Gas Chromatograph was used to do the study. Columns were made from 1/3 in. O.D. stainless steel tubing, between 1.5 ft. and 6.0 ft. in length, and were wound into compact helices. Coal samples with particle sizes of +60-80 mesh were used as packing in the columns.

A Valco manual injector was used to introduce gas samples into the carrier gas stream. The injector delivered a 25.0 μ l sample gas pulse. The detector was a Varian Thermoconductivity detector and was used in conjunction with a AutoLab System I Computing integrator and a Servocorder SR 6253 recorder.

Flow control was maintained by needle valves in the pneumatics cabinet of the Varian 3700 Gas Chromatograph. Flow rates of 15-30 cc/min, measured by an Alltech Flow Check, were used with a pressure drop across the column no greater than 35 psig. Hi-purity helium was used as the carrier gas and hi-purity nitrogen, carbon dioxide, oxygen, and dimethylether were used as gas samples. The nitrogen gas sample, which was inert towards the coal, was used to measure the dead-space time of the column.

Heat of Adsorption Determination. Retention time measurements were made for gas pulses of nitrogen, carbon dioxide, oxygen, and dimethylether. The Heat of Adsorption for each sample gas was determined using the equation proposed by Gale and Beebe,²

$$\log \alpha = \frac{\Delta H_i}{(2.303) RT_c} + A$$

with,

$$\alpha = \frac{(t_R - t_D)F \times 273}{T_f W}$$

where:

- α = slope of the initial linear portion of the isotherm
- ΔH_i = isotheric Heat of Adsorption
- R = Gas Constant
- T_c = Column Temperature
- A = Constant
- t_R = retention time of Adsorbent
- t_D = retention time of nonadsorbed gas
- F = carrier gas flow rate
- T_f = flow meter temperature

In this study, F was held constant at each column temperature and the effect of variation in T_f due to changes in room temperature was negligible. Therefore, plots of $\log(t_R - t_D)$ vs. $1/T_c$ were only necessary to determine the isosteric heats of adsorption for each sample gas.

²Gale, R. L. and Beebe, R. A., "Heats of Adsorption on Carbon Blacks and Bone Mineral," J. Phys. Chem., 68(3), 556-567 (1969).

CHAPTER 8

SULFUR EVOLUTION FROM COAL PARTICLES IN NONOXIDIZING ATMOSPHERES

8.1 OBJECTIVE AND MAIN FINDINGS

The objective of this task was to derive data on the quantity and rate of evolution of hydrogen sulfide from coal particles at conditions which simulate the initial stage of a LIMB burner and to relate the data to the distribution of the sulfur functionalities in the coals. Only limited data were derived up to this point, which do not permit a full characterization of the kinetics of sulfur evolution. Nevertheless, two major conclusions were arrived at:

1. the sulfur forms and functionalities influence very strongly the quantity and the rate of evolution of H_2S from a given coal
2. the fraction of sulfur evolved from -120 mesh coal particles in the "simulated reducing zones" tests never exceeded 18% of the original sulfur, for the coals tested.

The implications of these conclusions are far reaching since they indicate that: 1) No more than, say, 18% of the coal sulfur can be trapped in the reducing zone by EXTERNALLY ADDED limestone, even if all the conditions were ideal. (Calcium-containing materials, which are embedded in the coal, can trap additional sulfur in reducing conditions possibly by the reaction of COS with CaO.) 2) The performance of each coal in LIMB has to be optimized individually since different quantities of sulfur will be emitted from each coal and at different rates.

8.2 STRATEGY AND METHOD OF PERFORMANCE

The strategy of the study was to pyrolyze small amounts of well-characterized pulverized coal in conditions which to an extent simulate the initial part of the flight of a coal particle in a combustor.

The rate of evolution of hydrogen sulfide and the sulfur contents of the pyrolyzed coal were monitored in each experiment.

8.3 COALS OF THE STUDY

Tables 8.1 and 8.2 describe the sulfur forms and functional groups in the coals of the study. The sulfur forms were obtained by ASTM D2492 and the sulfur functionalities according to the method of Attar and Dupuis (1-5).

8.4 EXPERIMENTAL SYSTEM

The experimental system consists of three main parts: 1) a fluidized bed high-temperature reactor, 2) a solid and a gas feed system, and 3) a hydrogen sulfide detector. Figure 8.1 is a schematic diagram of the reaction system. The reactor is made of quartz and pyrex and its detailed description is given in Figure 8.2.

Two operational procedures were tried; the main difference between them was the presence or absence of silica powder in the reactor before injection of the coal. The presence of solid in a fluidized bed reactor improves the rate of heat transfer; however, in our case we did not observe any significant difference between sulfur evolution from coal samples heated with or without silica particles in the bed. Therefore, we stopped adding silica and most of the results were obtained without silica in the bed.

8.5 OPERATIONAL PROCEDURE

A typical operation consists of preheating the reactor to the desired reaction temperature while having nitrogen flowing through it. When the temperature is reached, an exact amount of coal, in the range of 0.2-0.5 gm is injected from the top and the rate of hydrogen sulfide evolution is followed using a hydrogen sulfide detector (modified Houston Atlas model 825A). The rate of hydrogen sulfide evolution is recorded on a high-speed recorder and subsequently analyzed. Calibration was done using pulses of 50 μ l of pure or diluted hydrogen sulfide. In order

TABLE 8.1 SULFUR FORMS IN THE COALS OF THE STUDY
(ASTM D2492)

Coal	Total S %	Pyritic S %	Sulfatic S %	Organic S %
A Kentucky #9, KY	4.23	2.12	0.21	1.90
B Illinois #6, Ill.	4.50	1.23	0.06	3.2
C Sulchi, Italy (lignitic)	6.50	0.70	0.02	5.78
D Gardenn, France (lignitic)	8.30	1.10	0.08	7.12
E Pittsburgh #8, Ohio	1.70	1.23	0.01	0.46
F Coalberg, W. Va.	2.29	1.39	0.02	0.88

TABLE 8.2 SULFUR FUNCTIONALITIES IN THE COALS OF THE STUDY¹
(Attar and Dupuis, 1-5; 10⁵ * moles S function/gm coal)

Coal	Thiols	Aryl Thiols	Aliphatic Sulfides	Aryl Sulfides	Simple Thiophenes	Complex Thiophenes
A ²	6.14	0.36	1.39	6.25	2.34	42.90
B	7.00	15.00	18.00	2.00	58 ⁽³⁾	
C	54.2	13.00	59.00 ⁽⁴⁾		54.00 ⁽³⁾	
D	77.8	21.30	47.00 ⁽⁴⁾		76.4 ⁽³⁾	
E	5.66	1.95	3.49	1.39	1.32	44.00
F			39.3	63.3	215	37.50

¹Determined in HCl-extracted coal.

²See Table 8.1 for description of coals.

³Includes complex thiophenes.

⁴Includes aryl sulfides.

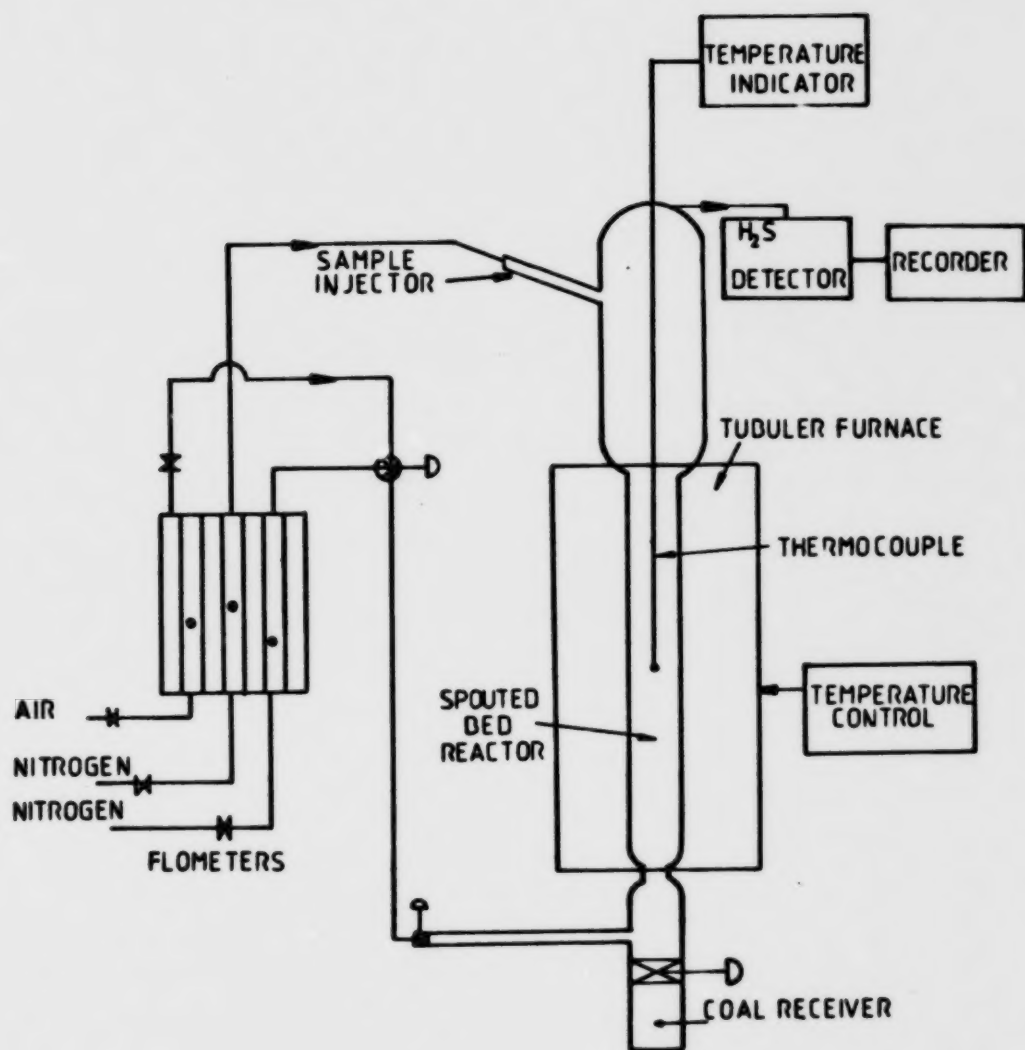


Figure 8.1 Schematic diagram of the reaction system

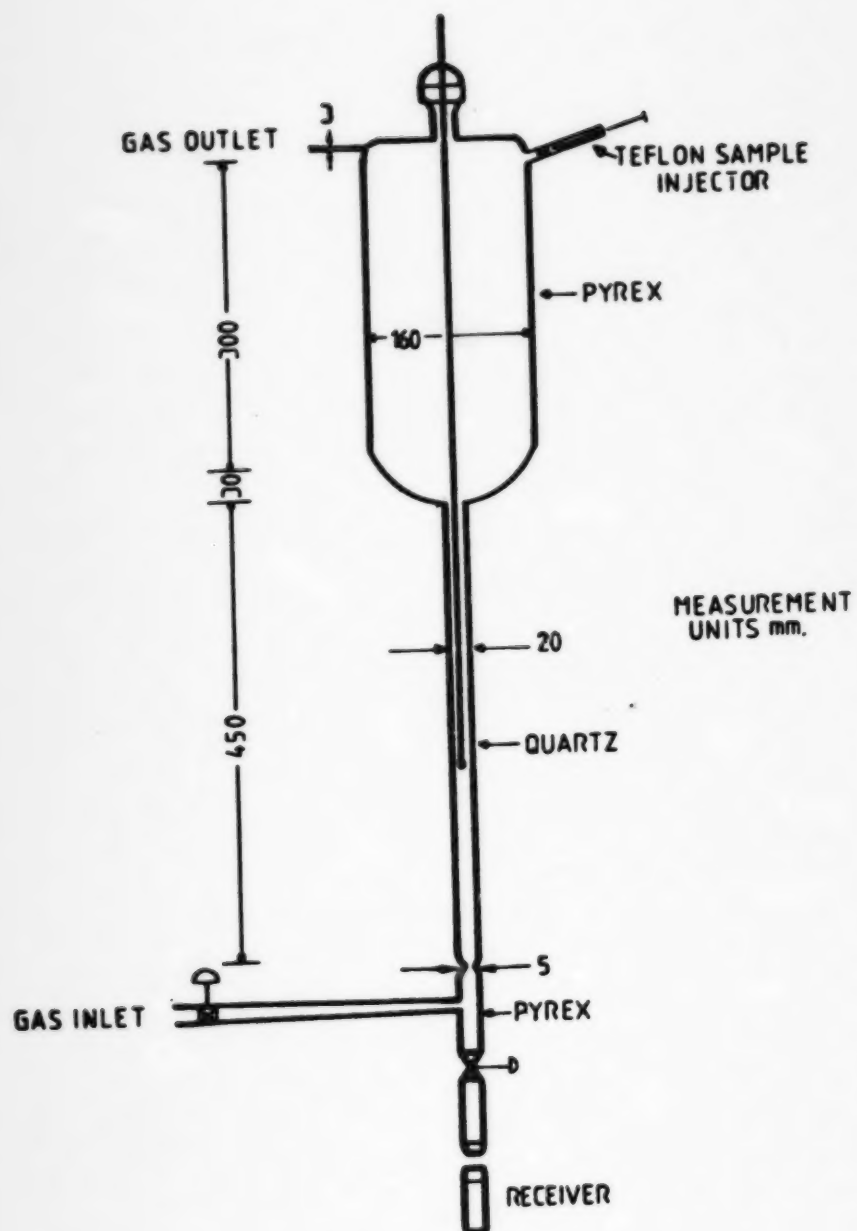


Figure 8.2 Coal decomposition reactor

to be able to quantitize the data, and because of the high sensitivity of the detector, the gaseous effluent had to be split and only part of it was channeled to the detector. The shape of the pulse of the pure hydrogen sulfide was used to infer the dispersion of gas due to the flow in the reactor and to calibrate the detector. The reaction system had to be cooled down and thoroughly cleaned between runs since small amount of tars left on cold walls adsorbed H_2S and created artificially long tails.

8.6 RESULTS AND DISCUSSION

Tables 8.3 and 8.4 show the fraction of the coal sulfur released at different reaction temperatures. Figures 8.3-8.14 show typical curves for the rate of evolution of hydrogen sulfide from two coals. In all these cases, -60+120 mesh coal particles were used and the cold gas flow rate was 60 ml/min. The recorder speed was 1"/min. Unfortunately, the quantity of coal injected had to be adjusted so that the complete peak will show up in the recording. The recorder speed appeared to be sufficient to record the rate of evolution of gases observed.

8.7 MATHEMATICAL MODELING OF SULFUR EVOLUTION

A zero-order model has been used to obtain a first-cut analysis of the rate of evolution of H_2S from coal particles injected to a hot gas. The basic assumptions of the model are:

1. the sulfur is present in distinct organic functionalities which decompose in a first-order reaction with well-defined preexponential factors and activation energies, i.e.:

$$-\frac{dF_i}{dt} = \frac{d[H_2S]_i}{dt} = k_{oi} e^{-E_i/RT} F_i \quad (8-1)$$

where F_i is the concentration of the i -th functionality and k_{oi} and E_i the preexponential factor and activation energy for its decomposition to H_2S .

2. the ambient temperature in the initial reducing stage is constant (T_0) and the heat transfer coefficient, h , obeys Eylin and Smith's

TABLE 8.3 FRACTION OF SULFUR VAPORIZED AS H_2S AT DIFFERENT TEMPERATURES

Temperature °C	% S Vaporized as H_2S -Illinois #6	% S Vaporized as H_2S -Kentucky #9
300	0.1	0.6
350	1.1	5.5
400	1.35	6.6
450	1.6	10.2
500	2.0	11.8

TABLE 8.4 FRACTION OF SULFUR VAPORIZED AS H_2S FROM DIFFERENT COALS AT 500°C

Coal	% S Vaporized as H_2S
A Kentucky #9, KY	11.8
B Illinois #6, Ill.	2.0
C Sulcy, Italy (lignitic)	18.9*
D Gardene, France (lignitic)	17.0*
E Pittsburgh #8, Ohio	13.0
F Coalberg, W.Va.	3.5

*These coals were first leached with HCl to remove the calcite from them. HCl extraction also opens the pores and exposes their surface and therefore enhances the rate of H_2S evolution.

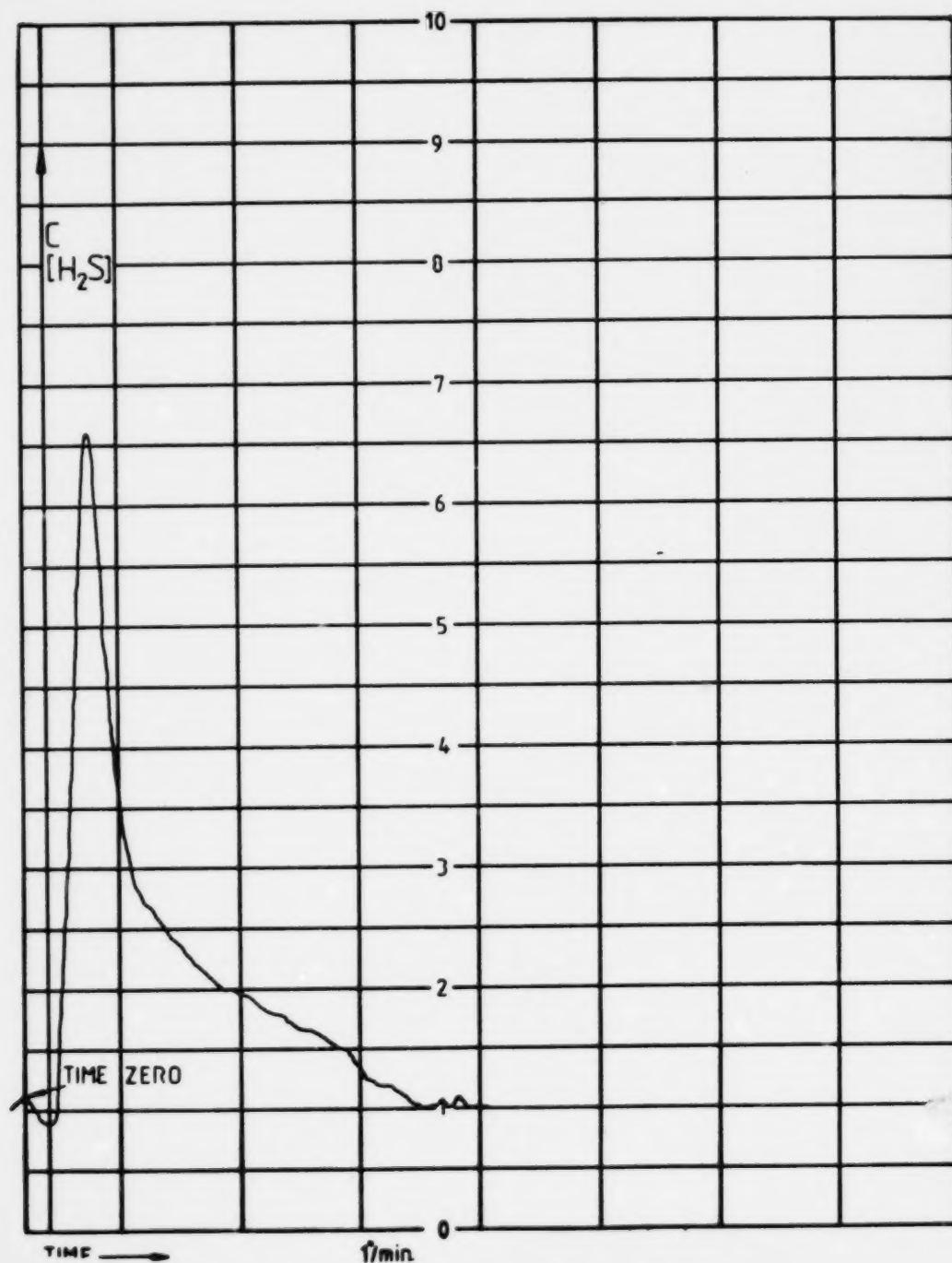
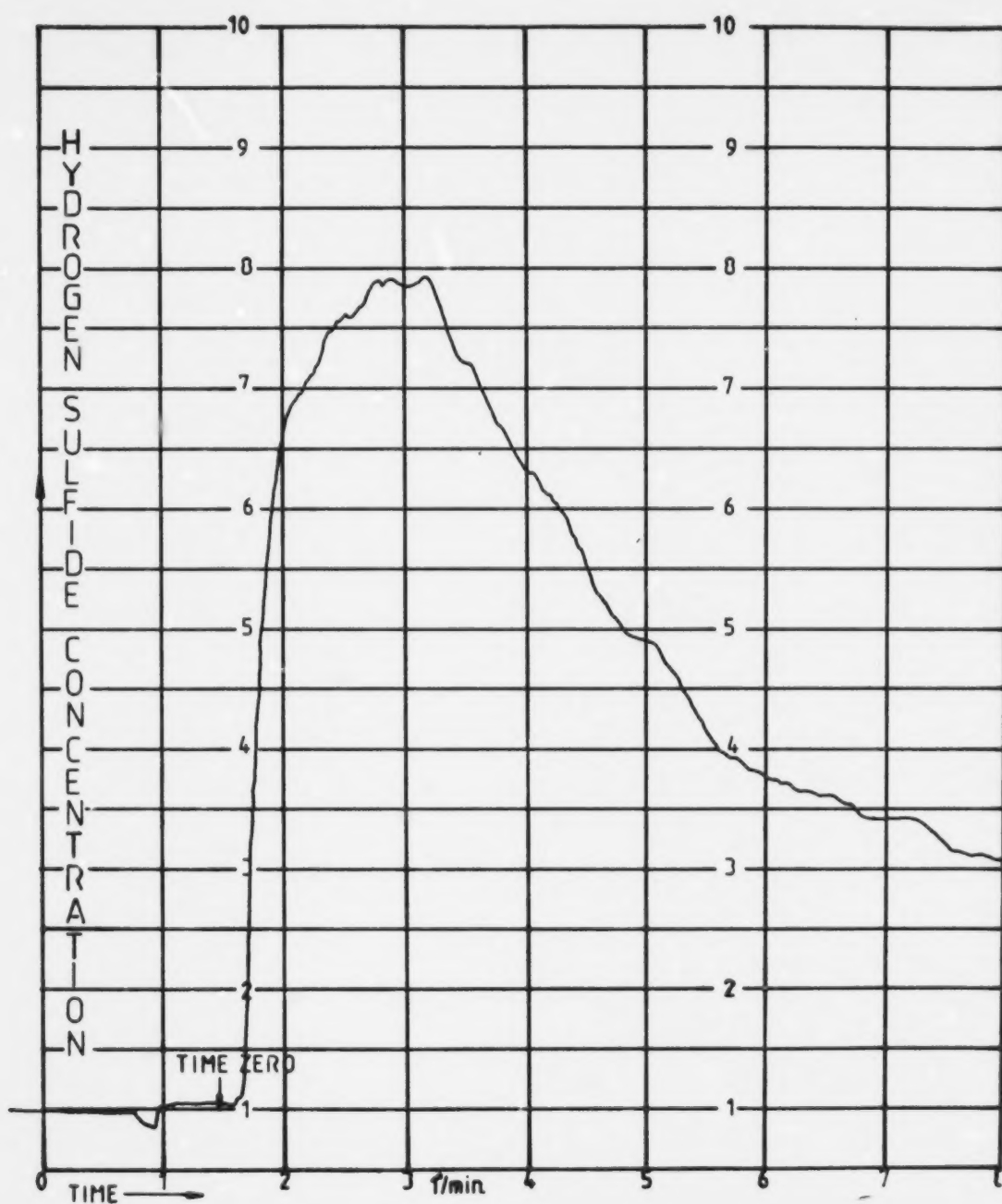


Figure 8.3 Calibration curve



FRENCH COAL GARDdene 400°C HCl TREATED

Figure 8.4 Rate of evolution of hydrogen sulfide from Garddene coal at 300°C

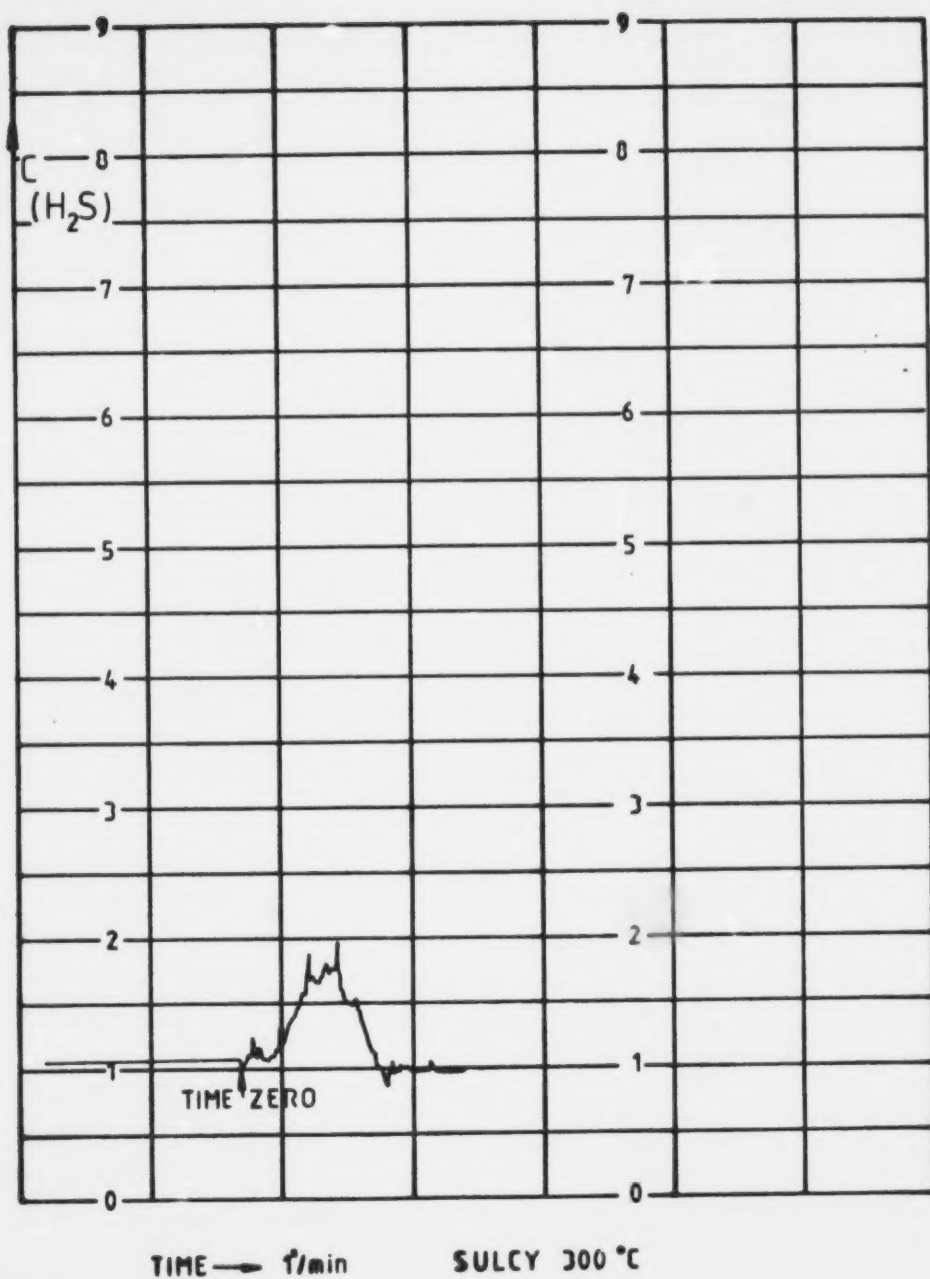


Figure 8.5 Rate of evolution of hydrogen sulfide from Sulcy coal at $300^\circ C$

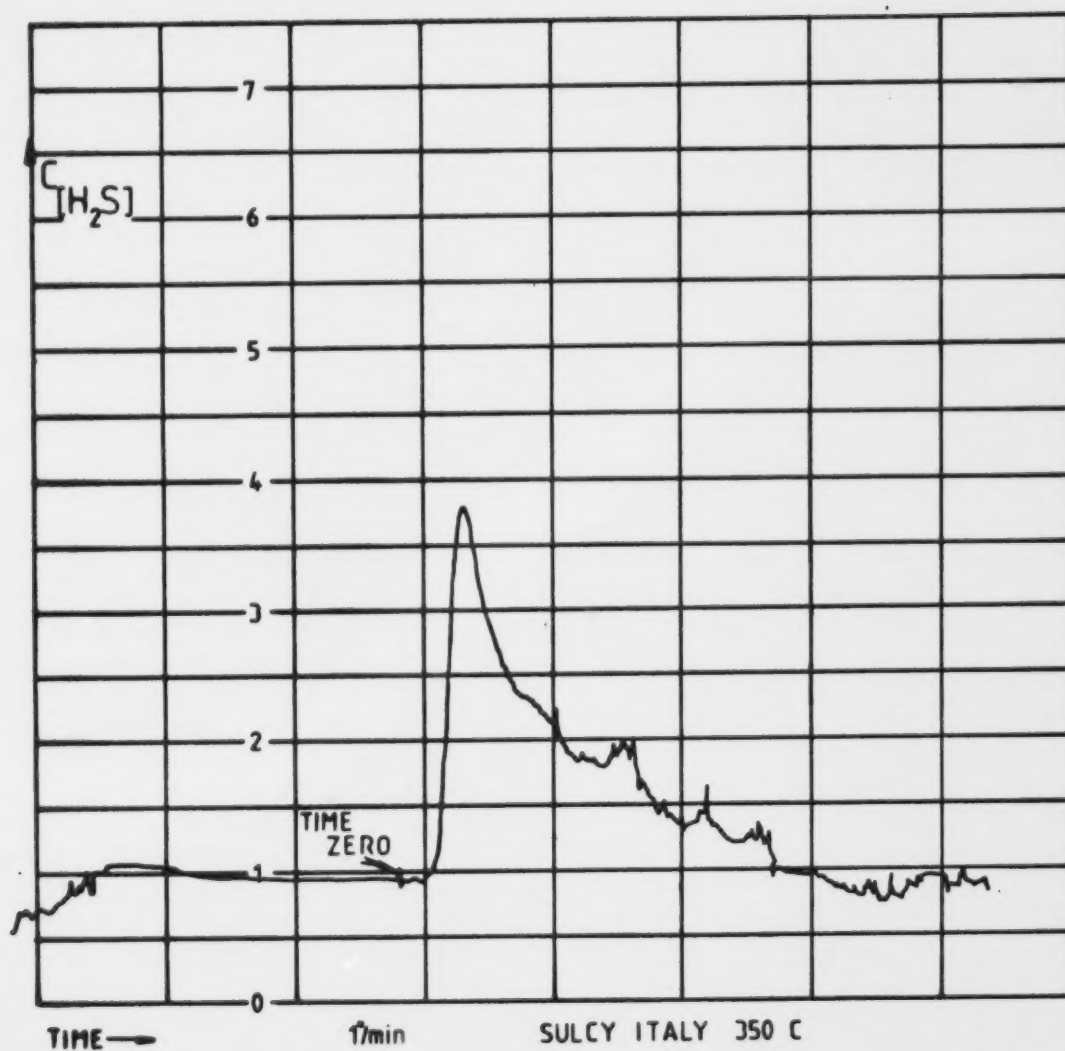


Figure 8.6 Rate of evolution of hydrogen sulfide from Sulcy coal at 350°C

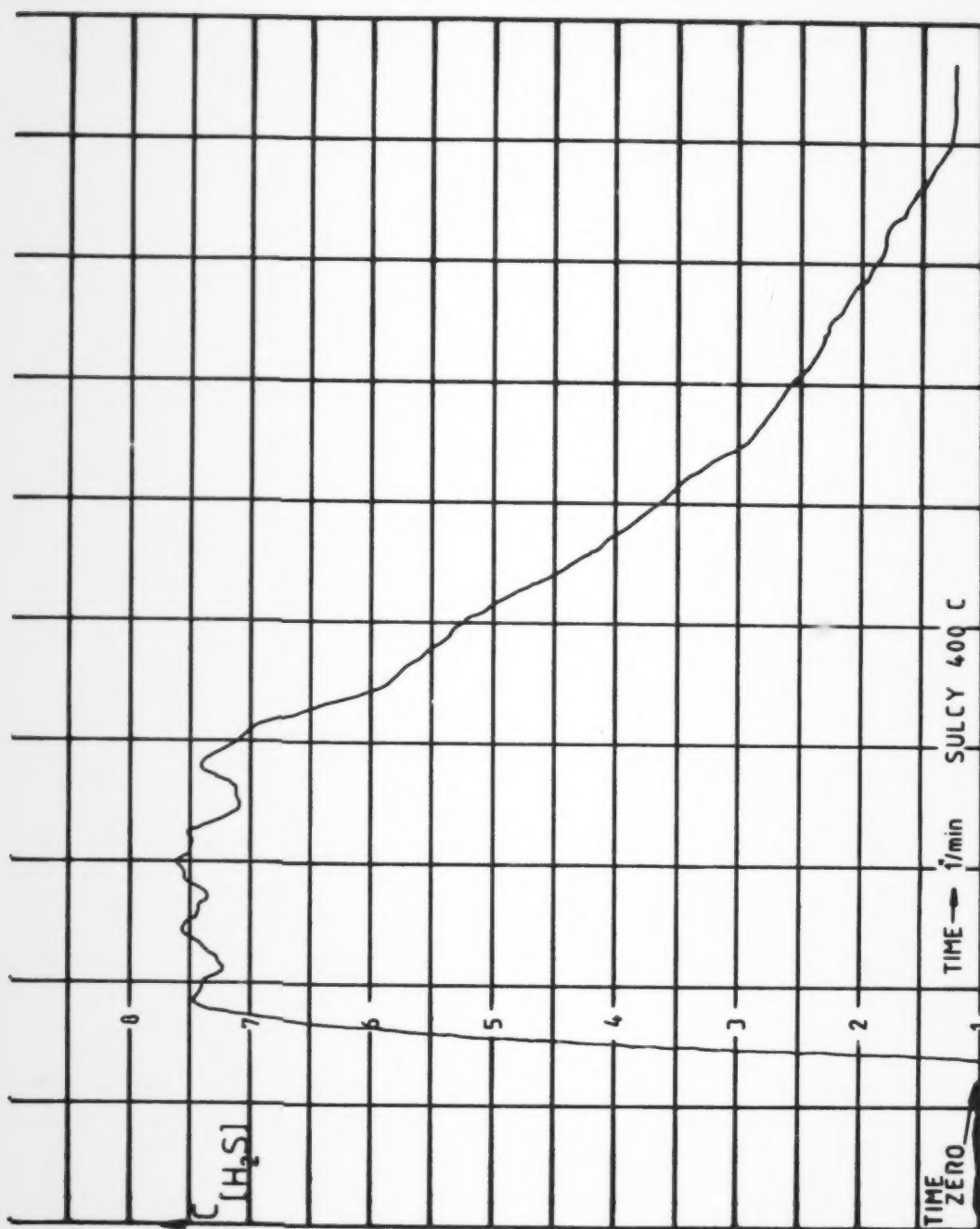


Figure 8.7 Rate of evolution of hydrogen sulfide from Sulcy coal at 400°C

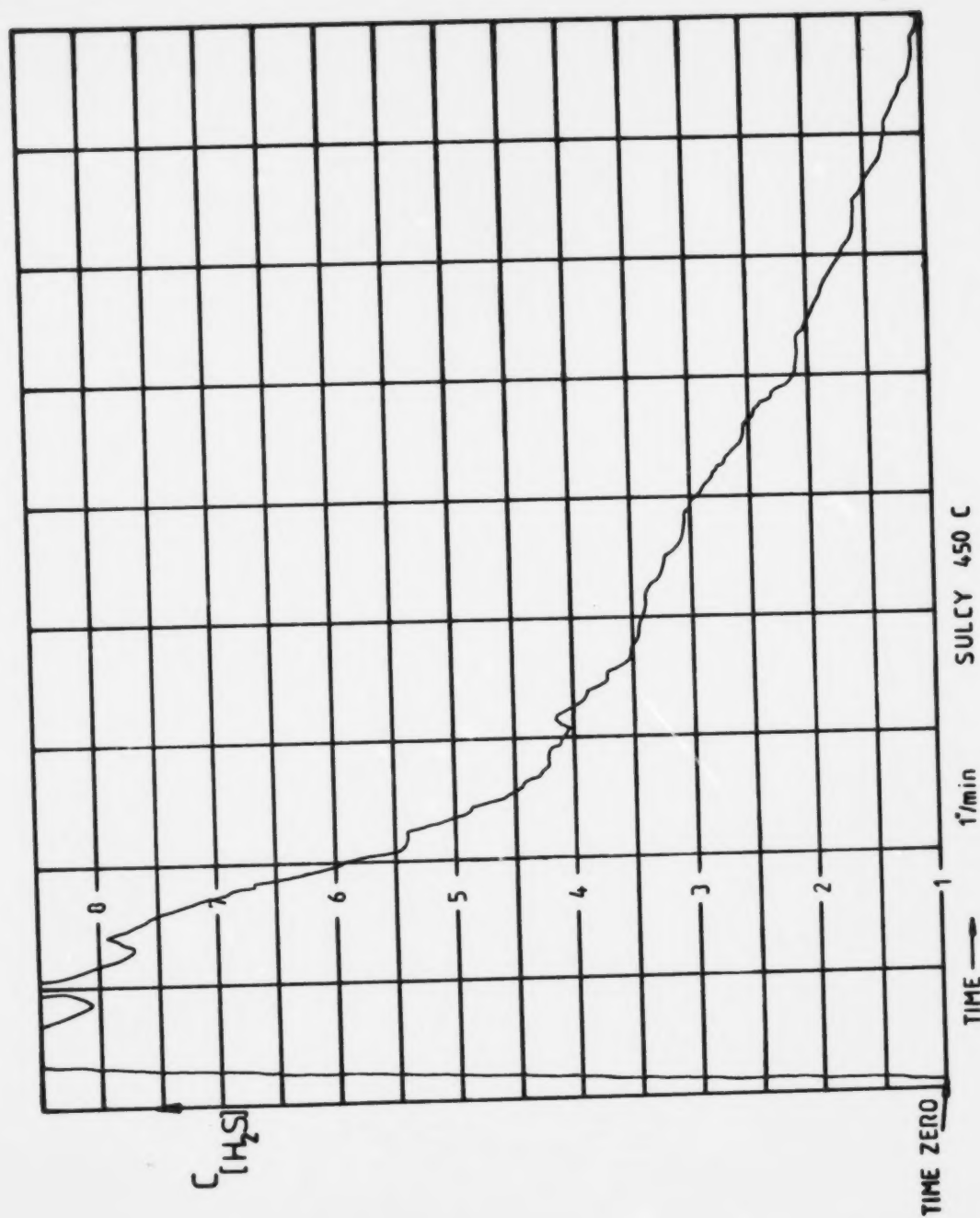


Figure 8.8 Rate of evolution of hydrogen sulfide from Sulcy coal at 450°C

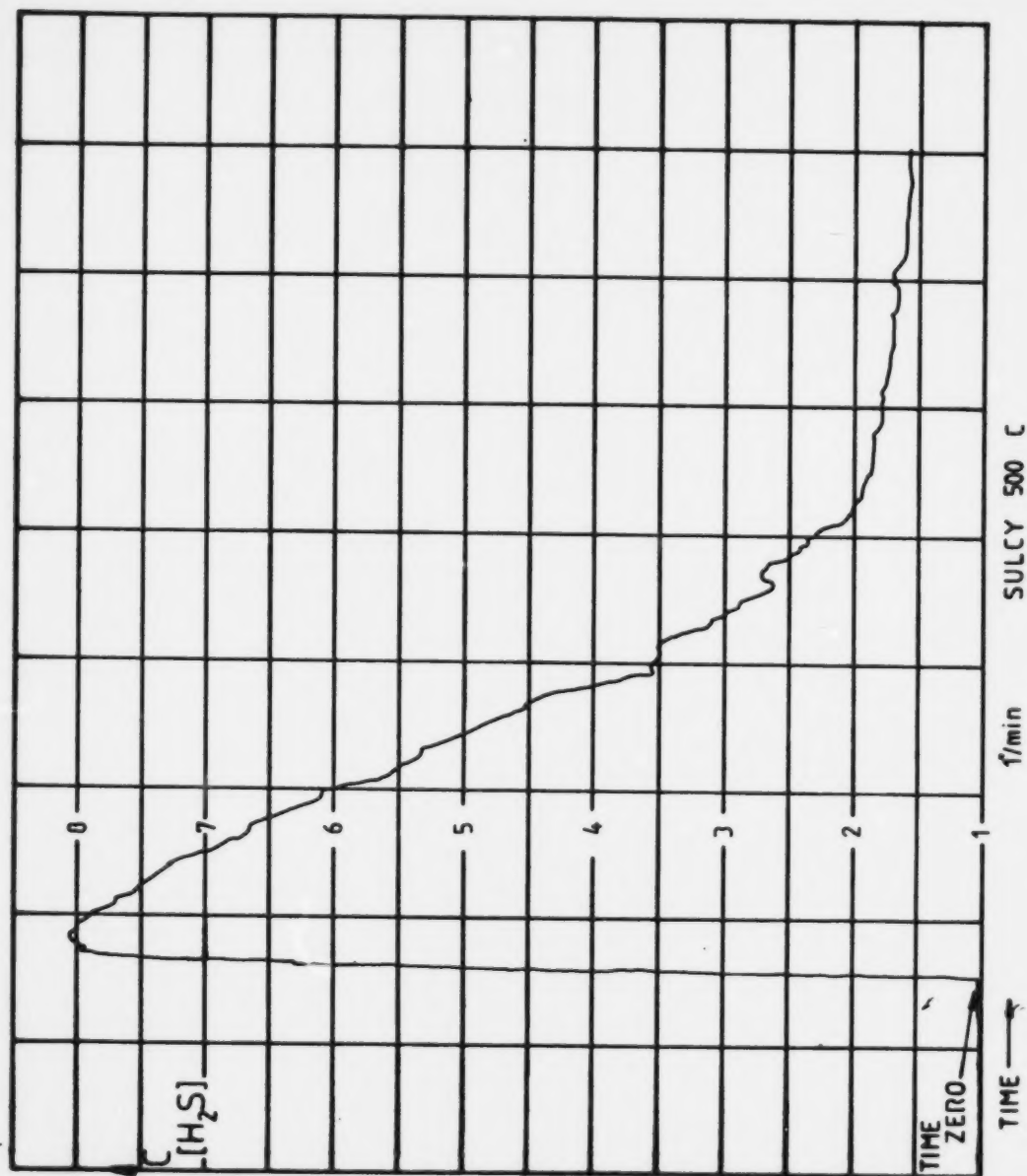


Figure 8.9 Rate of evolution of hydrogen sulfide from Sulcy coal at 500°C

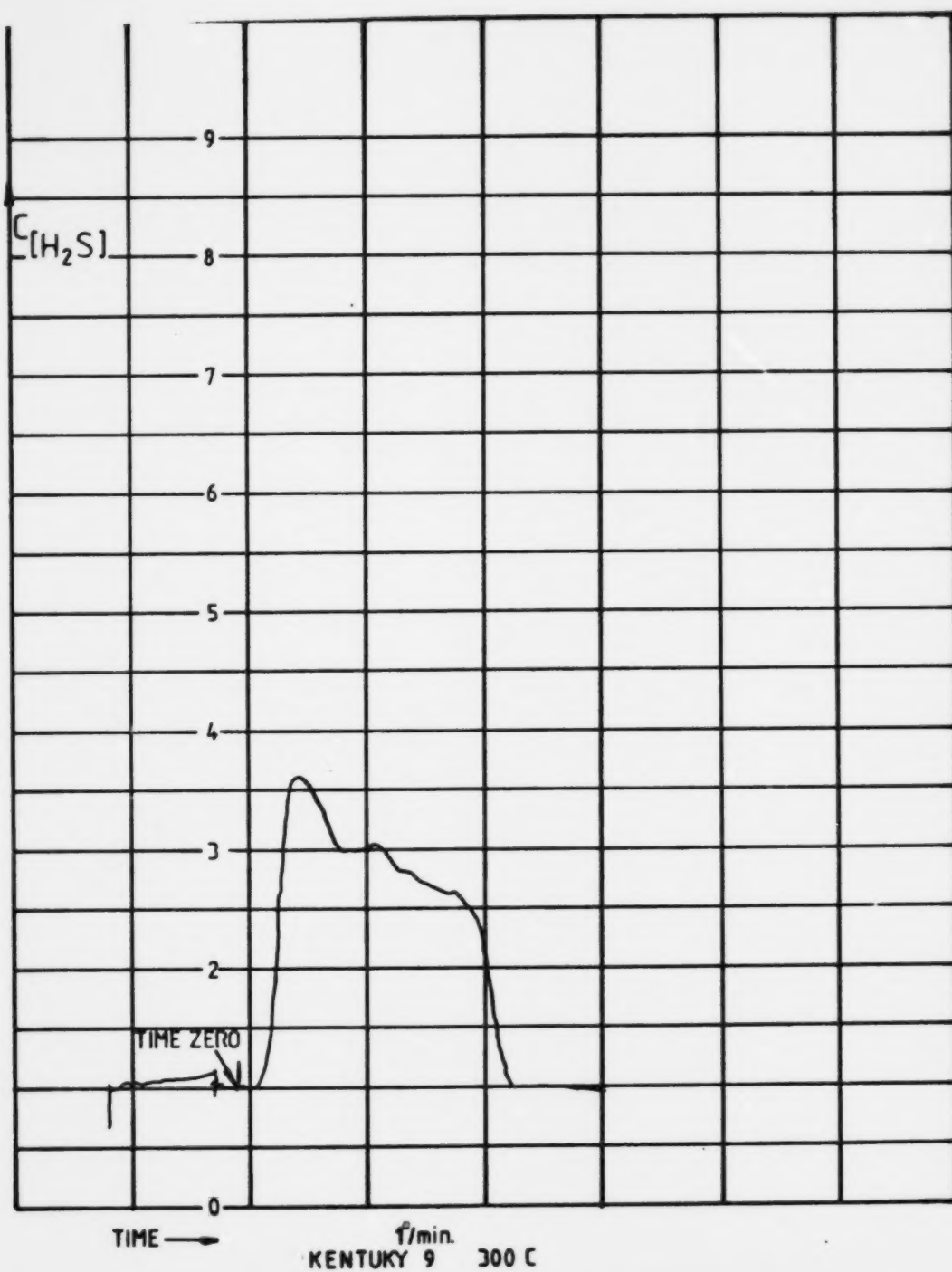


Figure 8.10 Rate of evolution of hydrogen sulfide from Kentucky #9 coal at 300°C

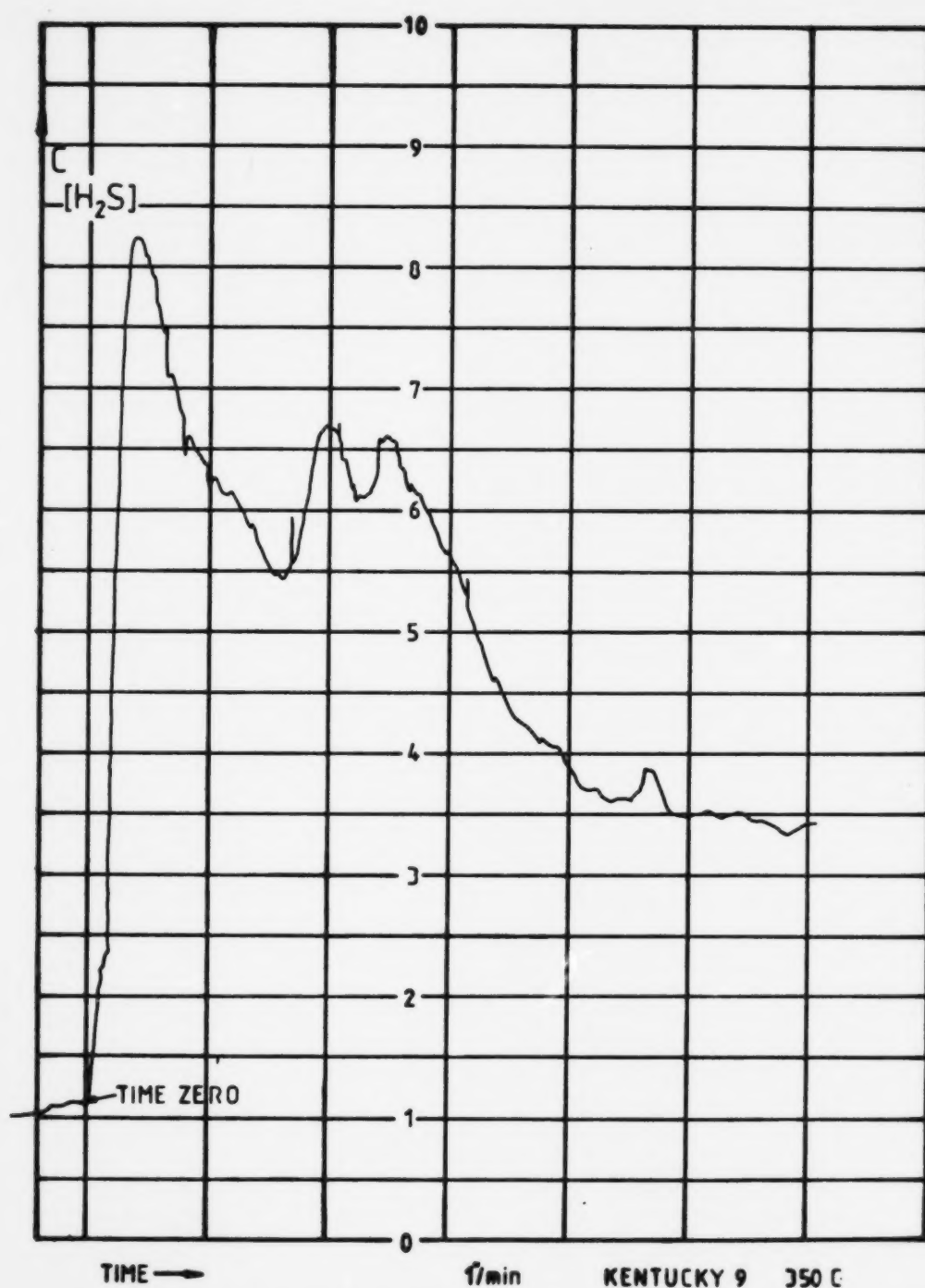


Figure 8.11 Rate of evolution of hydrogen sulfide from Kentucky #9 coal at 350°C

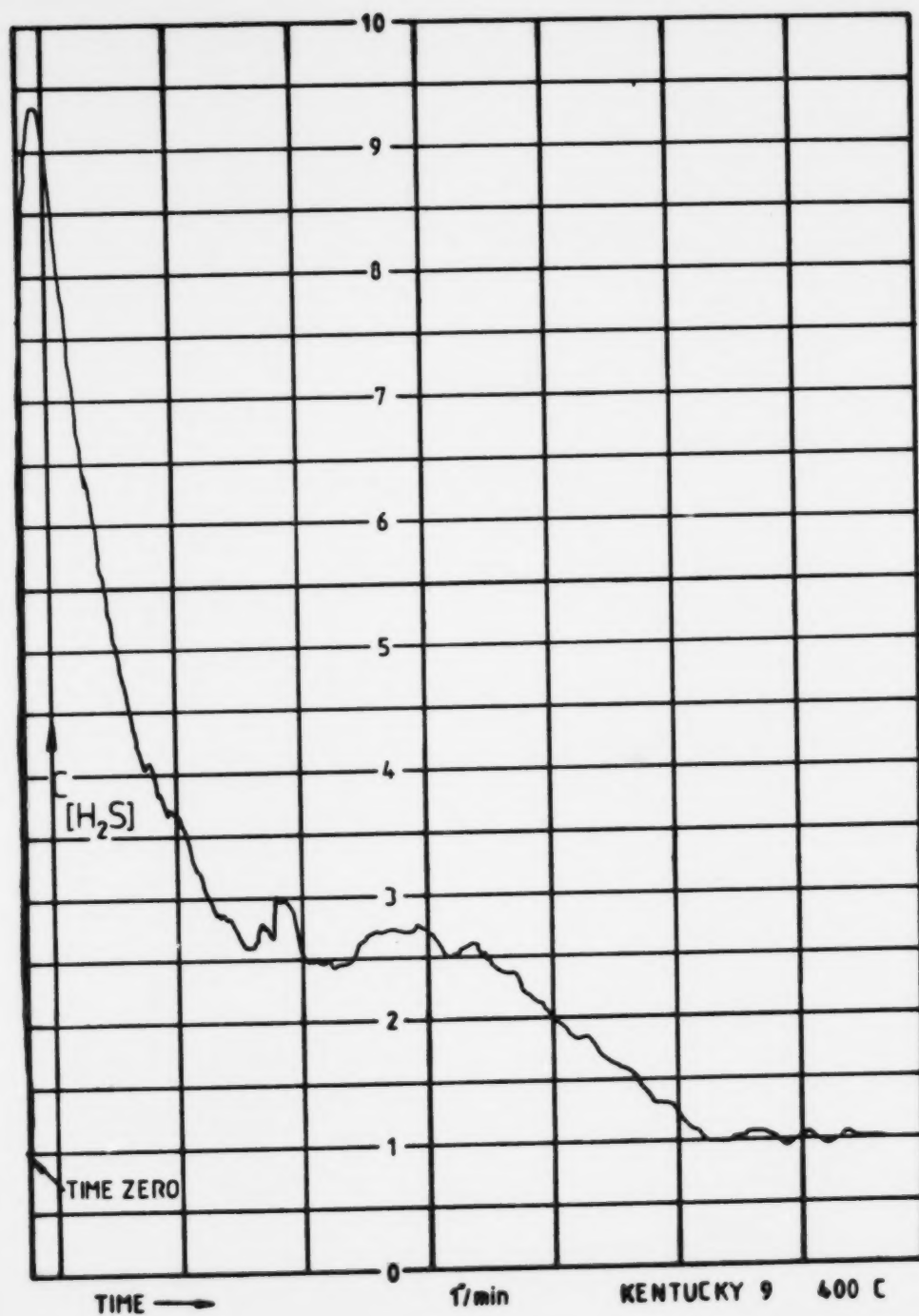


Figure 8.12 Rate of evolution of hydrogen sulfide from Kentucky #9 coal at 400°C



Figure 8.13 Rate of evolution of hydrogen sulfide from Kentucky #9 coal at 450°C

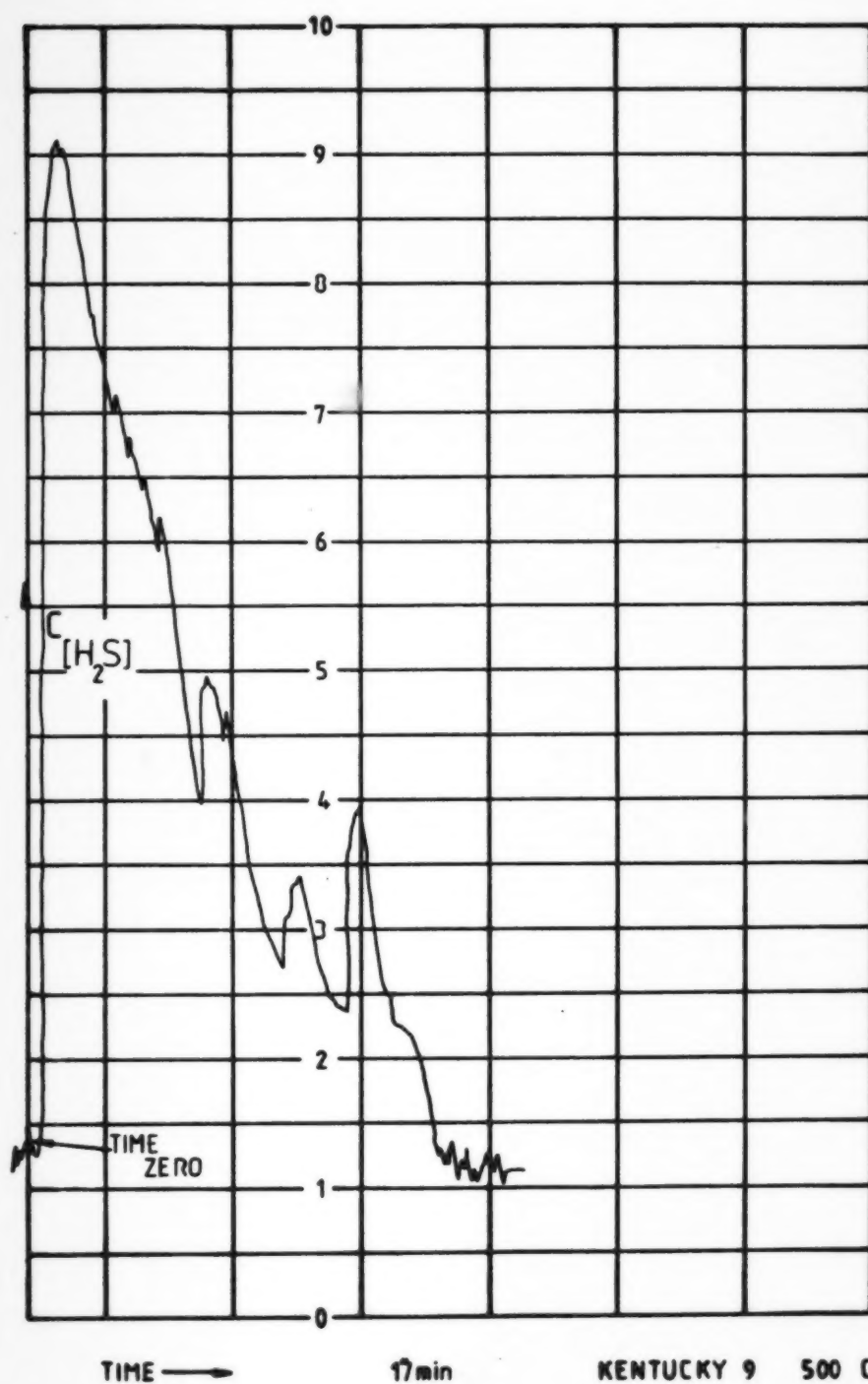


Figure 8.14 Rate of evolution of hydrogen sulfide from Kentucky #9 coal at 500°C

correlation:

$$h = \frac{C_1}{r} \left(\frac{T_0 + T}{2.273} \right)^{1.62} \quad (8-2)$$

where r is the particle radius and T its temperature. The decomposition reactions themselves are athermal.

3. the particles are spherical and maintain their shape and integrity during the initial first milliseconds. This assumption is the weakest one and will be improved in the next model.

Thus:

$$\rho C_p \frac{4\pi r^3}{3} \frac{dT}{dt} = h 4\pi r^2 (T_0 - T) \quad (8-3)$$

and in combination with (8-2)

$$\frac{dT}{dt} = \frac{3C_1}{\rho C_p r^2} (T_0 - T) \left(\frac{T_0 + T}{2.273} \right)^{1.64} = \alpha (T_0 - T) (T_0 + T)^{1.64} \quad (8-4)$$

where:

$$\alpha = \frac{3C_1}{\rho C_p r^2} \frac{1}{576^{0.64}} \quad (8-5)$$

For a constant α , equation (8-4) can be integrated analytically, provided that 1.67 is used instead of 1.64, to yield:

$$t = \frac{3}{2\alpha T_0} \left[-\frac{1}{2X^2} + \frac{1}{6a^2} \log \left(\frac{a^2 + ax + x^2}{(a-x)^2} \right) + \frac{1}{a^2\sqrt{3}} \text{ATN} \left(\frac{2x+a}{a\sqrt{3}} \right) - C_1 \right] \quad (8-6)$$

where:

$$X = (T + T_0)^3, \quad a = (2T_0)^{1/3}, \quad C_1 = \text{CONST.} \quad (8-7)$$

The concentration of H_2S in the effluent gas can be obtained by substituting equations (8-6) and (8-7) into the set of equations of type (1) for all the sulfur functional groups in the coal and integrating the differential equations. The final concentration is calculated from:

$$C = \sum_{i=1}^n \frac{w_{s_{oi}} k_i}{V} F_i e^{-E_i/RT} \quad (8-8)$$

where both F_i and T are functions of time. Figures 8.15 to 8.18 show the simulated effect of the distribution of sulfur functionalities on the rate of evolution of H_2S . The kinetic parameters used are the best we could devise for now from the data on the distribution of sulfur groups (Table 8.2) and the data of Figures 8.3 to 8.14 as well as reference 6. The curves are consistent with the experimentally observed data and demonstrate that the distribution of organic sulfur functionalities can influence the quantity and rate of hydrogen sulfide evolution and consequently the fraction that can react with calcium-containing materials in the fuel-rich reducing zone.

Figure 8.19 shows the effect of the combustor temperature on the rate of H_2S evolution. As expected, when the temperature is higher, the hydrogen sulfide will evolve over a shorter period of time. Note that, since lumped temperature and H_2S concentration were used in the formation of the model, and because the reverse H_2S trapping reaction was neglected, this model is just an approximation to the actual behavior. In a previous publication, we analyzed the rate of evolution of hydrogen sulfide from a single particle taking into account the reverse reaction and distributed concentration profile (Attar and Dupuis, 1981). Note that, since the reverse reaction which traps H_2S -sulfur back into the organic matrix was neglected in the present model, the integral of the curves is constant and independent of the temperature profile. However, in the model discussed by Attar and Dupuis (1981), the rate of heating will influence also the total amount of sulfur evolved. Since lumped temperature distribution is assumed in the present model, the rate of H_2S evolution will be influenced only via the rate of heat transfer to the particle. Thus, smaller particles heat faster and reach the maximum (combustor) temperature faster than larger particles. The difference between the curves is large, as demonstrated by Figure 8.20. The model has, however, to be improved to take the temperature profile into account, as far as combustion-type applications are concerned. The rate of temperature increase is described in Figure 8.21 for 4- μ particles.

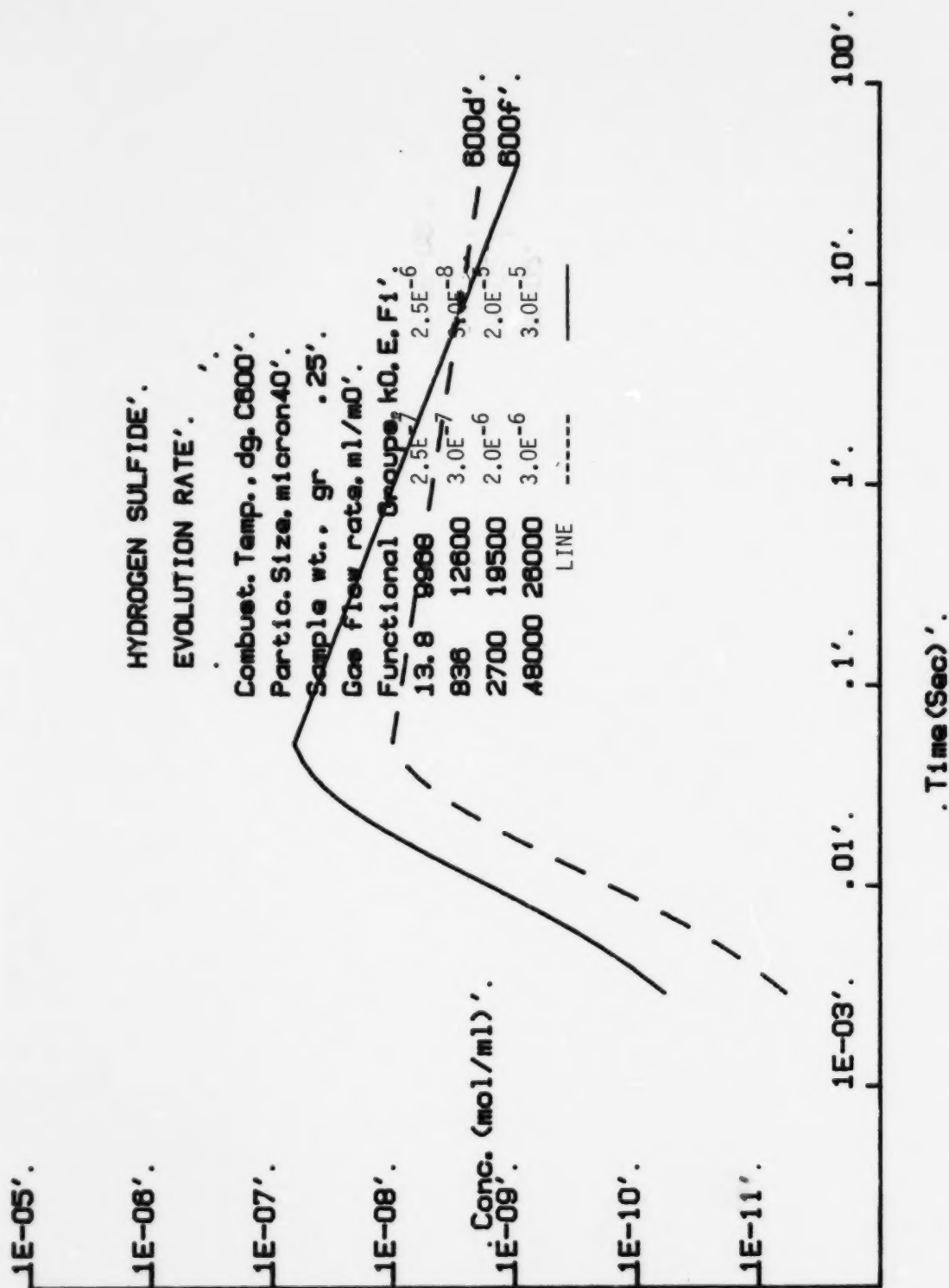


Figure 8.15 Effect of sulfur functional groups distribution on the rate of H₂S evolution at 600°C

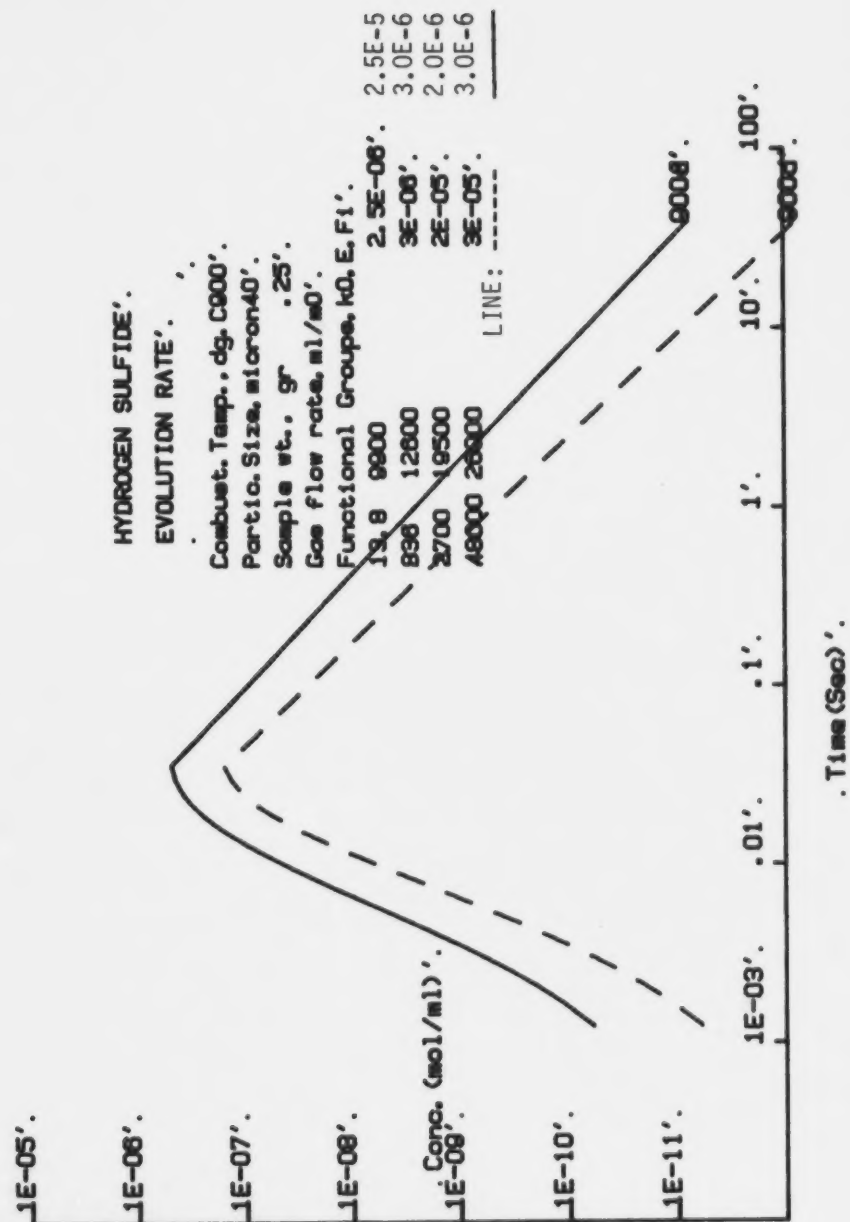


Figure 8.16 Influence of the initial distribution of sulfur groups on the rate of H_2S evolution at $900^\circ C$

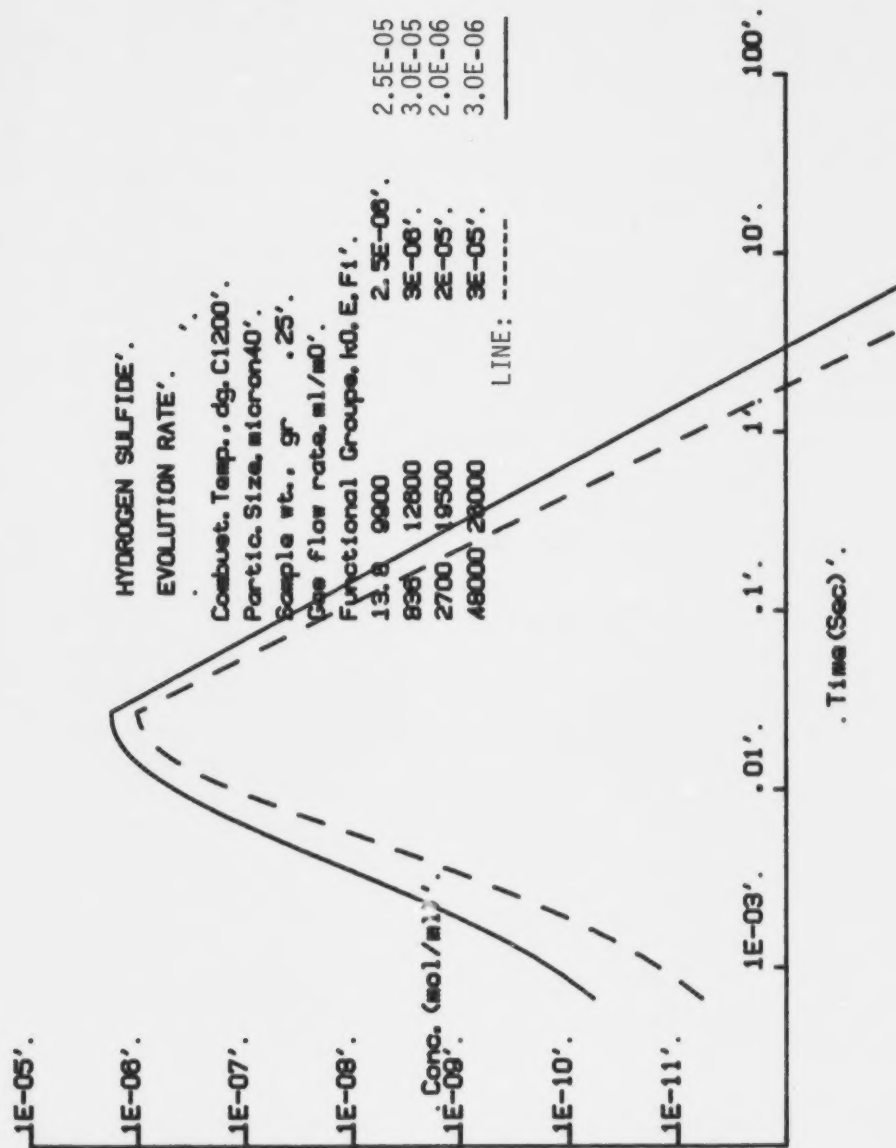


Figure 8.17 Influence of the initial distribution of sulfur groups on the rate of H_2S evolution at $1200^\circ C$

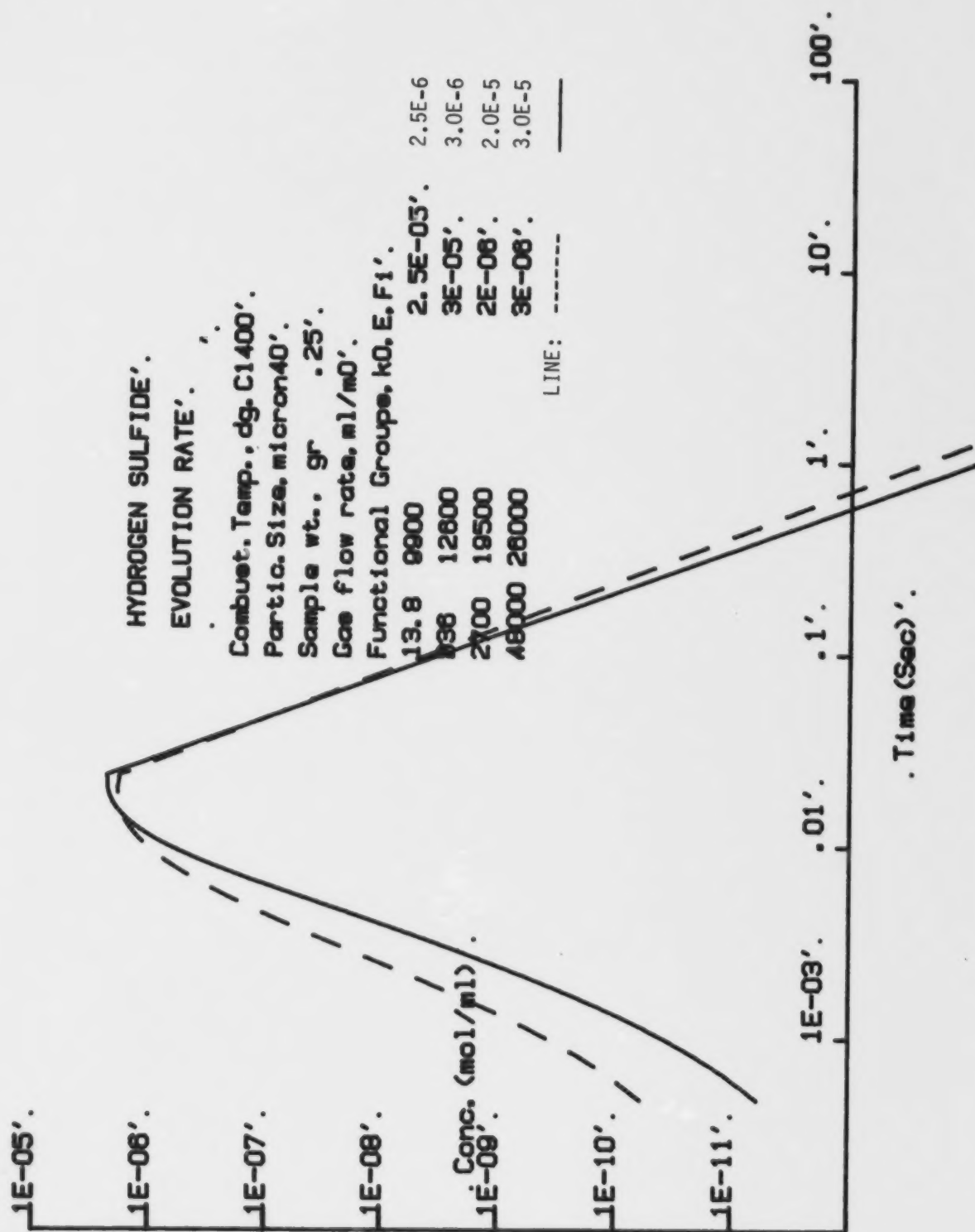


Figure 8.18 Influence of the initial distribution of sulfur groups on the rate of H_2S evolution at $1400^\circ C$

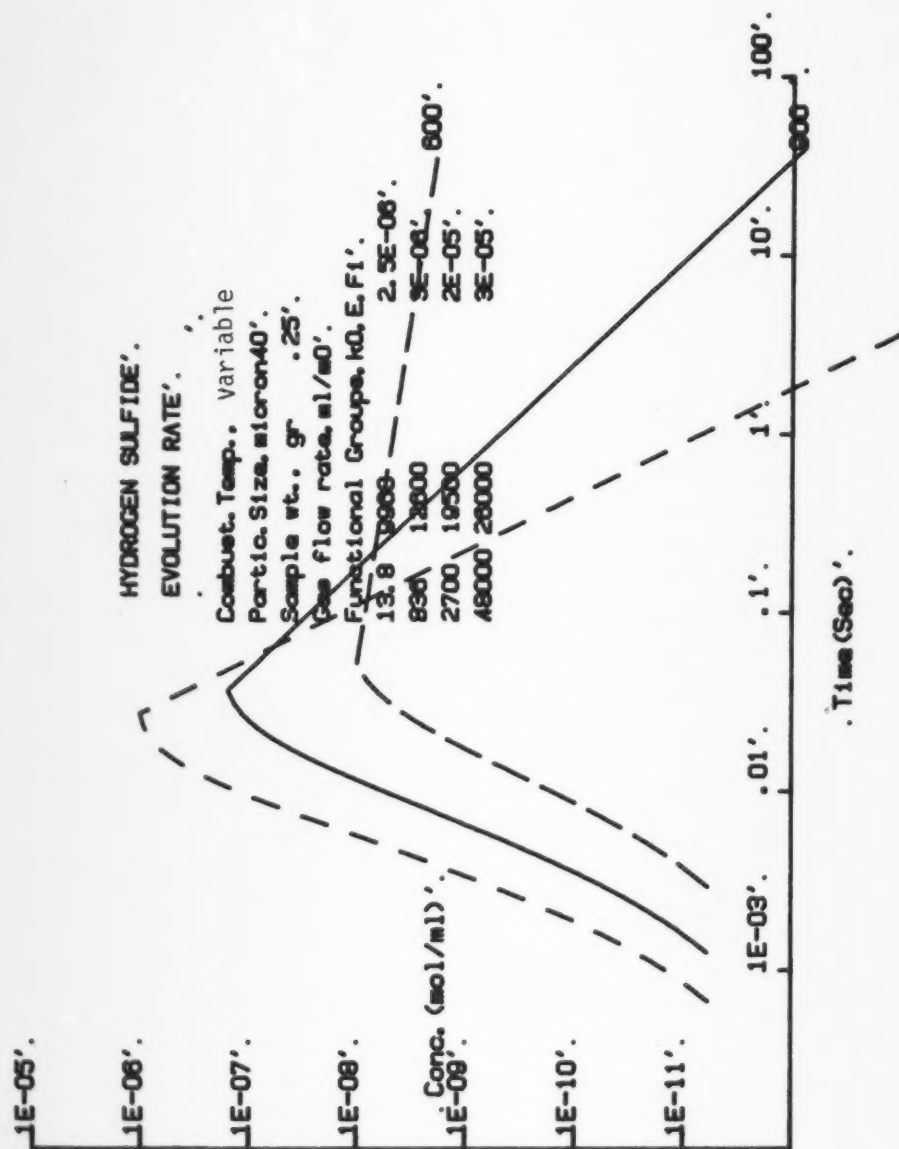


Figure 8.19 The effect of the reducing zone temperature on the rate of H_2S evolution

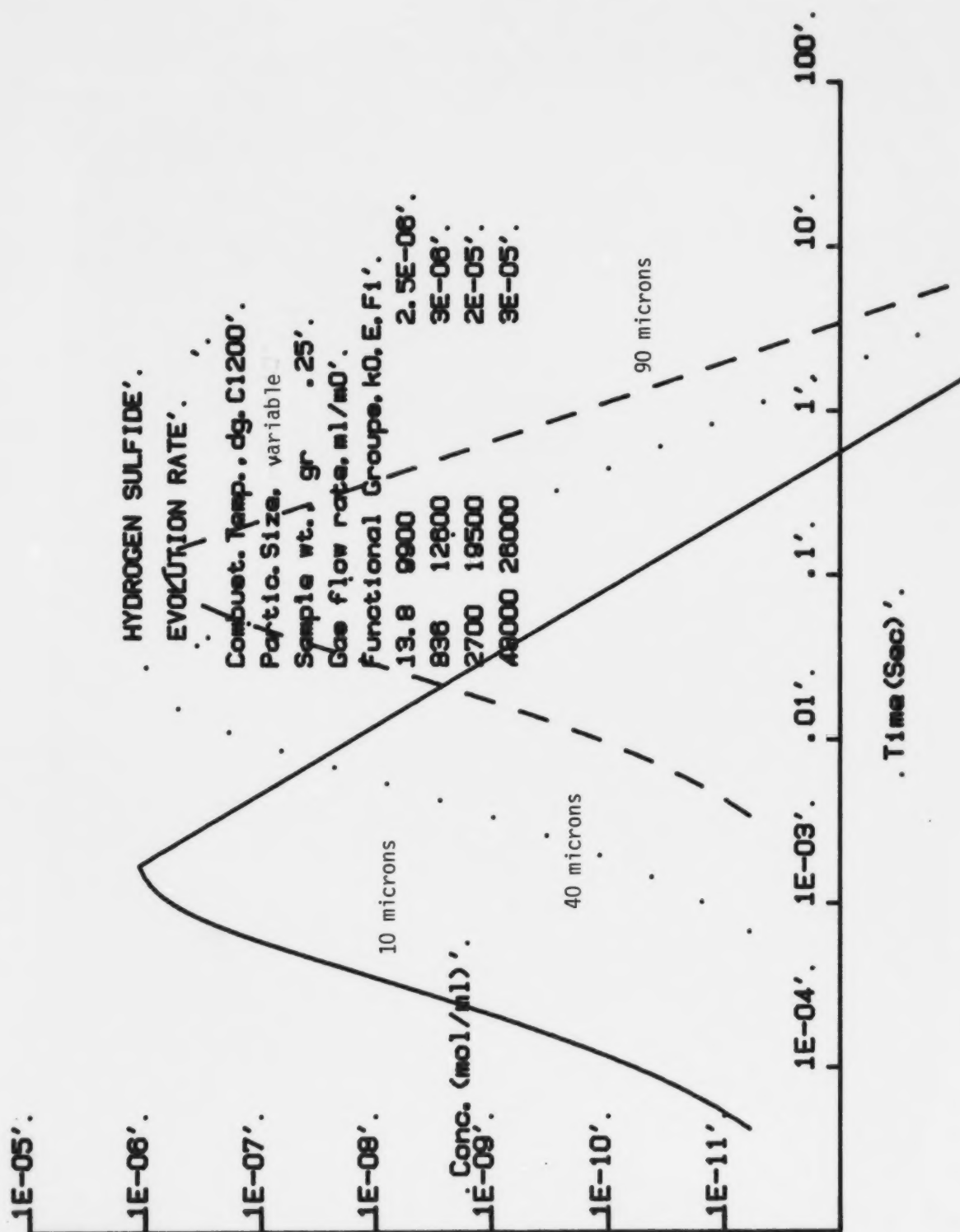
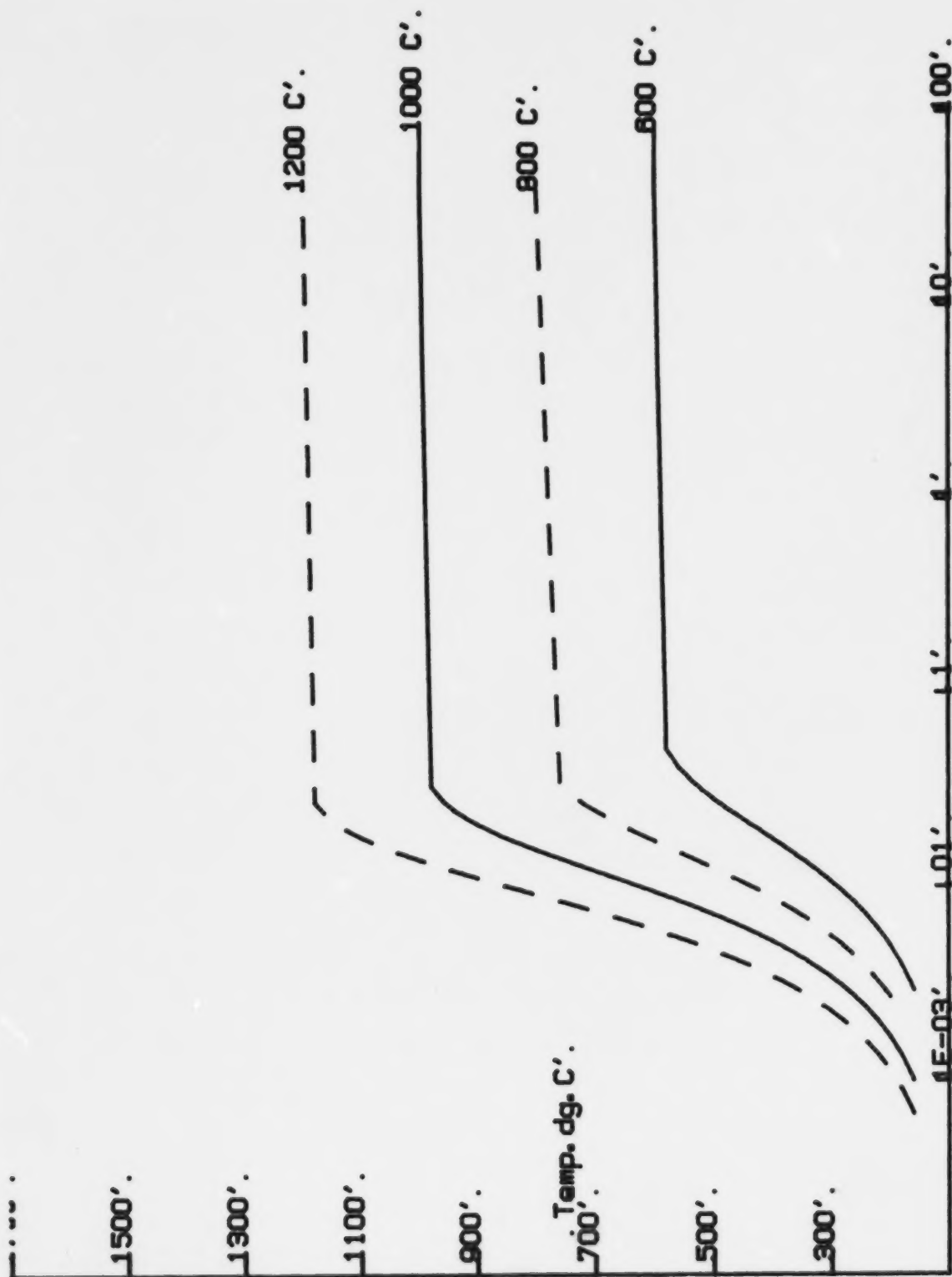


Figure 8.20 Effect of particle size on its rate of heating



. Time (Sec) '.

Figure 8.21 Rate of temperature increase of a 40-μ particle at different furnace temperatures

8.8 REFERENCES

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CHAPTER 9

NEUTRON ACTIVATION ANALYSIS (NAA)

OF LIMESTONE AND ASH SAMPLES

It is desired to know the role of impurities in catalyzing or inhibiting the rate of reaction of H_2S or SO_2 with the solid sample. Therefore, a detailed analysis of the raw and of sized fractions of Freedonia Valley limestone, of Georgia Texas limestone and of several coal ashes was conducted. For the description of the NAA method, see Appendix to this chapter.

9.1 OBJECTIVE

Characterize the chemical and impurities structure of the limestone samples to be used and of selected coal ash samples.

9.2 ACCOMPLISHMENTS

Three narrow-size fractions of Freedonia Valley limestone and the raw unfractionated material were analyzed. Also, samples of seven coal ashes of Georgia Texas limestone and two samples of calcined Georgia limestone were analyzed. The data are listed in Tables 9.1, 9.2 and 9.3. The data of Table 9.1 indicate clearly that the impurities are segregated and are more concentrated in the fine fraction. For example, the potassium, iron and zinc contents of the 8-12 micron fraction are 2-3 times larger than that of the "as received" material. Since iron is known to catalyze the reaction of limestone with H_2S and SO_2 , the specific reactivity of the 8-12 micron material (mole/sec cm^2 surface) may appear smaller than that of the larger limestone particles because of the larger concentration of catalytically-active impurities, provided that they are distributed homogeneously in the solid matrix. This will partially compensate for the difference in the total specific external surface area of small and large limestone particles.

TABLE 9.1 NAA OF FREEDONIA VALLEY LIMESTONE
(MICROGRAM ELEMENT/GM)

Element	As Received	Smaller than 1 micron	4-8 microns	8-12 microns
Mercury	<0.1	<0.01	<0.01	<0.01
Samarium	0.25 ± 3%	0.40 ± 3%	0.52 ± 3%	0.59 ± 3%
Uranium	0.60 ± 5%	1.10 ± 5%	1.41 ± 5%	1.50 ± 5%
Lanthanum	1.37 ± 2%	1.32 ± 1%	1.61 ± 1%	2.09 ± 1%
Cadmium	<2.0 ±	2.34 ± 8%	1.48 ± 8%	2.54 ± 8%
Gold	<0.01 ±	<0.0005	<0.0005	<0.0005
Arsenic	0.18 ± 30%	0.62 ± 1%	0.69 ± 1%	2.96 ± 0.5%
Antimony	0.02 ± 20%	0.24 ± 5%	0.55 ± 5%	1.50 ± 1%
Bromine	0.64 ± 1%	0.62 ± 2%	0.60 ± 2%	1.61 ± 1%
Sodium	63.61 ± 3%	91.72 ± 1%	172.08 ± 1%	246.34 ± 1%
Potassium	460.18 ± 25%	291.48 ± 10%	321.89 ± 10%	925.73 ± 10%
Cerium	1.37 ± 20%	1.18 ± 10%	1.20 ± 10%	1.65 ± 10%
Calcium	321,193 ± 1%	<1000.0	<1000.0	<1000.0
Selenium	<0.5	<1.50	<1.53	<2.18
Thorium	0.11 ± 5%	0.087	0.10 ± 5%	0.24 ± 5%
Chromium	6.16 ± 10%	5.77 ± 10%	5.66 ± 10%	10.29 ± 10%
Europium	0.01 ± 10%	<0.025	<0.033	0.06 ± 5%
Ytterbium		0.14 ± 10%	0.15 ± 10%	0.15 ± 10%
Barium	53.62 ± 20%	<21.66	<34.66	<32.96
Cesium	<0.01	<0.051	< 0.074	< 0.12 ± 10%
Silver	<0.01	<2.54	< 2.44	< 3.83
Nickel	74.95 ± 10%	<25.0	<25.0	<25.0
Scandium	0.20 ± 1%	0.18 ± 5%	0.16 ± 5%	0.39 ± 5%
Rubidium	<4.0	< 4.99	< 4.77	10.48 ± 10%
Iron	1144.44 ± 2%	1164.70 ± 1%	867.51 ± 1%	2218.30 ± 1%
Zinc	56.12 ± 20%	1336.40 ± 3%	1193.30 ± 3%	3277.70 ± 3%
Cobalt	0.24 ± 5%	0.33 ± 1%	0.28 ± 1%	0.99 ± 1%

TABLE 9.2 COMPOSITION OF GEORGIA LIMESTONE AND ITS CALCINES
(MICROGRAM ELEMENT/GM SAMPLE)

Element	Lime--As Received	Calcined in spouted bed at 780°C	Calcined in a crucible at 780°C
Barium	34.05 ± 25%	45.40 ± 20%	14.09 ± 30%
Titanium	273.72 ± 10%	319.87 ± 10%	489.10 ± 10%
Iodine	< 10.0	< 10.0	< 10.0 ±
Manganese	114.40 ± 1%	3.08 ± 2%	249.91 ± 1%
Magnesium	10,278.29 ± 10%	10,473.68 ± 10%	23,390.13 ± 10%
Copper	< 50.0 ±	< 50.0	< 50.0
Sodium	62.97 ± 3%	71.90 ± 3%	118.97 ± 3%
Vanadium	11.82 ± 3%	13.19 ± 3%	26.05 ± 3%
Chlorine	< 100.0 ±	< 100.0	< 100.0 ±
Aluminum	3218.31 ± 0.5%	3635.42 ± 0.5%	6543.05 ± 0.5%
Mercury	< 0.1	< 0.0	< 0.0
Samarium	0.44 ± 3%	0.44 ± 1%	0.60 ± 1%
Cerium	2.45 ± 10%	3.20 ± 20%	3.14 ± 20%
Uranium	1.18 ± 3%	1.52 ± 3%	2.12 ± 3%
Selenium	< 0.5	< 0.5	< 0.5
Thorium	0.38 ± 3%	0.53 ± 3%	0.61 ± 3%
Chromium	3.56 ± 10%	4.11 ± 10%	5.94 ± 10%
Lanthanum	1.13 ± 2%	1.38 ± 2%	1.79 ± 2%
Cadmium	2.90 ± 10%	2.82 ± 10%	4.11 ± 10%
Gold	< 0.001	< 0.001	< 0.001
Arsenic	1.58 ± 2%	2.01 ± 5%	2.84 ± 5%
Antimony	0.12 ± 5%	0.17 ± 2%	0.21 ± 2%
Silver	< 0.01	< 0.01	< 0.01
Bromine	0.93 ± 1%	1.12 ± 1%	1.50 ± 1%
Scandium	0.39 ± 1%	0.48 ± 1%	0.60 ± 1%
Rubidium	4.0	5.30 ± 20%	4.86 ± 20%
Iron	2041.73 ± 1%	2257.64 ± 1%	3279.17 ± 1%
Zinc	< 100.0	< 100.0	< 100.0
Cobalt	0.60 ± 5%	0.75 ± 5%	0.78 ± 5%

TABLE 9.2 (CONTINUED)

Element	Lime--As Received	Calcined in spouted bed at 780°C	Calcined in a crucible at 780°C
Potassium	451.33 ± 25%	530.97 ± 20%	1141.59 ± 20%
Calcium	308,233 ± 1%	349,834 ± 1%	463,255 ± 1%
Europium	0.03 ± 10%	0.02 ± 10%	0.01 ± 10%
Cesium	0.17 ± 5%	0.17 ± 5%	0.19 ± 5%
Nickel	77.14 ± 10%	85.14 ± 10%	107.81 ± 10%
Molybdenum	2.83 ± 5%	5.34 ± 5%	7.39 ± 5%

TABLE 9.3 NAA OF TRACE ELEMENTS IN ASHES
(µGRAMS ELEMENT/GRAM MATRIX)

Element	Texas Lignite Wilcox	Low Sulfur Bituminous Coal W. Va.	High Sulfur Bituminous Coal, Ohio	Lower Kittanning West Virginia	Upper Freeport	Nerco Subbituminous	Pittsburgh #8
Barium	1225.05 ± 1%	7304.50 ± 1%	362.82 ± 3%	791.98 ± 1%	603.33 ± 1%	17,027.79 ± 0.5%	1566.73 ± 1%
Titanium	8550.64 ± 1%	7650.00 ± 1%	9465.38 ± 1%	15,567.95 ± 1%	9792.31 ± 1%	9085.91 ± 1%	6070.51 ± 1%
Iodine	<10.0	<10.0	<10.0	<10.0 ±	<10.0	<10.0	<10.0
Manganese	1036.18 ± 0.5%	271.17 ± 1%	123.13 ± 1%	339.74 ± 1%	244.24 ± 1%	357.92 ± 1%	513.81 ± 1%
Magnesium	8927.6 ± 10%	11,571.05 ± 10%	10,742.76 ± 10%	12,340.13 ± 10%	10,087.50 ± 10%	18,269.74 ± 10%	10,790.13 ± 10%
Copper	<150.0	<150.0	<150.0	<150.0	<150.0	<150.0	<150.0
Sodium	892.62 ± 0.5%	1870.49 ± 0.5%	663.65 ± 0.5%	1631.29 ± 0.5%	1100.04 ± 0.5%	37,401.94 ± 0.1%	6086.12 ± 0.5%
Vanadium	146.22 ± 1%	222.14 ± 1%	122.77 ± 1%	237.96 ± 1%	183.24 ± 1%	190.30 ± 1%	127.49 ± 1%
Chlorine	<100.0	<100.0	<100.0	<100.0	<100.0	<100.0	<100.0
Aluminum	66,060.5 ± 0.1%	151,371.02 ± 0.1%	120,999.66 ± 0.1%	154,425.93 ± 0.1%	137,702.37 ± 0.1%	109,535.42 ± 0.1%	85,984.07 ± 0.1%
Mercury	<0.1 ±	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Samarium	5.53 ± 1%	9.71 ± 1%	4.17 ± 1%	7.22 ± 1%	5.86 ± 1%	4.97 ± 1%	5.56 ± 1%
Cerium	106.25 ± 10%	197.11 ± 5%	141.23 ± 5%	185.56 ± 5%	161.50 ± 5%	115.89 ± 5%	132.27 ± 5%
Uranium	5.45 ± 2%	5.49 ± 2%	3.92 ± 2%	4.20 ± 2%	4.03 ± 2%	8.27 ± 2%	4.79 ± 2%
Selenium	1.86 ± 5%	<0.5	1.93 ± 5%	3.23 ± 5%	<0.5	<0.5	<0.5
Thorium	18.49 ± 0.5%	19.31 ± 0.5%	20.89 ± 0.5%	26.48 ± 0.5%	20.58 ± 0.5%	13.40 ± 0.5%	10.56 ± 0.5%
Chromium	103.98 ± 1%	314.67 ± 1%	276.81 ± 1%	378.92 ± 1%	346.50 ± 1%	575.47 ± 1%	204.05 ± 1%
Lanthanum	49.98 ± 0.3%	85.33 ± 0.3%	51.35 ± 0.3%	82.57 ± 0.3%	67.47 ± 0.3%	42.24 ± 0.3%	45.43 ± 0.3%
Cadmium	17.83 ± 10%	<2.0	2.95 ± 10%	<2.0	2.63 ± 10%	8.89 ± 10%	13.88 ± 10%
Gold	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Arsenic	14.13 ± 2%	56.01 ± 1%	13.72 ± 2%	23.50 ± 1%	40.01 ± 1%	31.26 ± 1%	46.01 ± 1%
Antimony	2.96 ± 0.5%	3.43 ± 0.5%	0.60 ± 1%	2.09 ± 0.5%	1.86 ± 0.5%	4.31 ± 0.5%	1.55 ± 0.5%

TABLE 9.3 (CONTINUED)

Element	Texas Lignite Wilcox	Low Sulfur Bituminous Coal, W. Va.	High Sulfur Bituminous Coal, Ohio	Lower Kittanning West Virginia	Upper Freeport	Nerco Subbituminous	Pittsburgh #8
Silver	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bromine	0.82 ± 1%	3.05 ± 1%	1.08 ± 1%	1.23 ± 1%	1.76 ± 1%	0.1	0.77 1%
Scandium	18.61 ± 0.1%	29.82 ± 0.1%	22.75 ± 0.1%	35.43 ± 0.1%	30.98 ± 0.1%	21.91 ± 0.1%	14.51 ± 0.1%
Rubidium	46.56 ± 10%	200.27 ± 5%	146.48 ± 5%	163.31 ± 5%	153.87 ± 5%	42.28 ± 10%	40.78 ± 10%
Iron	69,184.73 ± 0.5%	50,919.48 ± 0.5%	140,011.82 ± 0.1%	57,254.17 ± 0.5%	67,552.21 ± 0.5%	3159.92 ± 1%	206,461.30 ± 0.1%
Zinc	<100.0	<142.73	<100.00	144.20 ± 10%	<100.0	<100.0	<100.0
Cobalt	43.01 ± 0.1%	63.30 ± 0.1%	34.04 ± 0.1%	32.69 ± 0.1%	34.33 ± 0.1%	22.26 ± 0.1%	23.16 ± 0.1%
Potassium	8203.54 ± 15%	24,097.3 ± 5%	18,017.7 ± 5%	20,442.4 ± 5%	15,964.6 ± 5%	300.0	6141.59 ± 15%
Calcium	43,118 ± 10%	27,112 ± 10%	28,102 ± 10%	29,084 ± 10%	21,800 ± 10%	106,831 ± 1%	38,520 ± 10%
Europium	1.68 ± 1%	3.47 ± 1%	1.88 ± 1%	2.70 ± 1%	1.94 ± 1%	2.04 ± 1%	1.29 ± 1%
Cesium	1.94 ± 2%	5.95 ± 1%	4.99 ± 1%	3.66 ± 1%	3.98 ± 1%	3.17 ± 1%	1.22 ± 1%
Nickel	<50.0	<50.0	<50.0	<50.0	<50.0	148.67 ± 10%	<50.0
Molybdenum	<0.5	<0.5	<0.5	<0.5	<0.5	33.95 ± 1%	<0.5

Table 9.2 shows that differences in the concentration of impurities exist between samples calcined in a spouted bed and those calcined in a crucible, despite the fact that the original material was the same -120+230 mesh limestone. The major reason is that the limestone fractures and the fines elutriate from the spouted bed while the main reaction in the crucible is the decomposition of the carbonate and loss of CO_2 . The marked differences in the concentration of key elements like Ca, Fe, Mg and K have to be considered when comparing analytical results obtained in a flow reactor vs. a fixed bed reactor.

Table 9.3 shows the elemental composition of ashes of seven different coals. The variation in the composition of the ashes is great as expected. In general, the lower ranked coals have more Ca, K, Mg and Na in their ashes than the higher ranked coals. In addition, the high sulfur coals have more iron in the ashes, due to the conversion of FeS_2 to Fe_2O_3 .

9.3 APPENDIX: NAA OF COAL ASH AND LIMESTONE SAMPLES

Neutron activation analysis is a very sensitive method for the determination of the chemical composition of materials. The application of the method consists of the following steps:

1. Irradiation of the sample with neutrons which activate the nuclei.
2. Monitoring for a period the rate of emission of γ -radiation from the sample a length of time t_0 after the irradiation, counting separately the flux of γ at specific energies.

Since each element absorbs neutrons with a different cross-section, σ_i , different amounts, A_{i0} , of initially radioactive atoms are formed in the irradiation.

$$A_{i0} = C_i K \sigma_i F_n \quad (9-1)$$

where F_n is the flux of neutrons, C_i is the concentration of the i -th element and K is a constant which depends on the sample shape and to a lesser extent on the other components. The decay process is a first order reaction of the form:

$$A_i \rightarrow P_i + \gamma_i \quad (9-2)$$

Therefore, the rate of formation of γ_i with energy E_i , $\frac{dn_{\gamma_i}}{dt}$ is:

$$-\frac{dA_i}{dt} = k_i A_i = \frac{dn_{\gamma_i}}{dt} \quad (9-3)$$

$$\text{or: } A_i = A_{i0} e^{-k_i t_0} \quad (9-4)$$

Thus, if the sample is monitored for a period θ , one obtains:

$$\begin{aligned} \frac{dn_{\gamma_i}}{dt} &= k_i A_{i0} e^{-k_i t_0} = k_i K \theta C_i \sigma_i e^{-k_i t_0} \\ n_{\gamma_i} &= K \theta C_i \sigma_i \left[e^{-k_i t_0} - e^{-k_i (t_0 + \theta)} \right] \end{aligned} \quad (9-5)$$

In reality, not all the γ_i emitted are monitored; thus, a calibration factor, B_i , is needed to allow quantitation of the data. The method is very sensitive for most heavy elements but is not so sensitive for the light ones. The Nuclear Energy Services at NCSU uses for coal ash the following parameters:

Irradiation period: 20 sec. for the active elements and 4 hr. for the less active or less abundant elements.

Neutron flux: $1.5 \cdot 10^{13}$ n/cm²sec.

Monitoring: 200-100 sec. on a scintillator of GeLi with 24% efficiency and Ortec with 25% efficiency. The accuracy achieved for each element is noted near its value.

CHAPTER 10

ASH FUSION TEMPERATURE: A THERMODYNAMIC-BASED MODEL WHICH APPLIES TO HIGH AND TO LOW CALCIUM ASH

10.1 ABSTRACT

The paper describes a thermodynamically based correlation for coal ash fusion temperature and ash composition. The basic assumption used is that since ash composition variations around some "average ash composition" are not too large, the effect of concentration differences from the average ash composition of different ash components will be independent of each other and will influence the ash fusion temperature in a Van't Hoffen type way. Data from the literature were used to obtain the values of parameters which best describe the data. A seven-parameter correlation is proposed which permits predicting the ash fusion temperature with accuracy of $\pm 50^{\circ}\text{C}$ or better.

10.2 INTRODUCTION

Coal ash characteristics strongly influence boiler design parameters and they influence the type and amount of fouling, slagging, and the ash disposal techniques and air pollution. One key characteristic is the temperature range at which ash softens and melts. Since ash is a heterogeneous mixture, some ash particles melt at lower temperatures than others, giving ash a range of progressive fusion temperatures. ASTM D-1857 (1) "FUSIBILITY OF COAL AND COKE ASH" defines the analytical tests to determine the initial deformation temperature (IDT), the softening temperature (ST) and the fluid temperature (FT) of a prepared ash.

Several empirical techniques have been developed to predict the fouling and slagging characteristics of the ash from the ash fusion temperatures (2,3).

The subject of this paper is a new method to predict ash fusion temperatures. The proposed method is based on thermodynamic reasoning; thus, it is not surprising that it allows the predictions of the ash fusion temperatures of a large range of coal sources with a reasonable accuracy from a simple formula with few parameters.

Being able to predict ash fusion temperatures is useful when burning coal blends is considered or, for example, when it is desired to predict the ash fusion temperature of ash-limestone mixtures. (Limestone is often added to coal as means to control sulfur pollution.) Previous attempts to develop correlations to predict ash fusion temperatures were essentially empirical and often used secondary variables like the weight percent oxide as a basis of the correlation.

10.3 MODEL BASIS

The thermodynamics of ideal dilute binary solutions relate the mole fraction of a solute to the melting temperature according to the freezing point depression equation (4).

$$\ln (1-x_i) = \frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (10-1)$$

where x_i is the mole fraction of the solute, ΔH is the heat of fusion of the pure solvent at absolute temperature T_0 , R is the gas law constant and T is the absolute melting temperature of the mixture.

Re-arranging the equation:

$$\frac{1}{T} = \frac{1}{T_0} + \frac{R}{\Delta H} \ln (1-x_i) \quad (10-2)$$

yields the reciprocal melting temperature due to the perturbation of the pure substance with x_i mole fraction of i .

Two key approaches can be used to construct and predict the ash melting temperature of a multicomponent system: A) by successively adding one component at a time and evaluating its effect on the fusion temperature of the extant mixture, and B) by simultaneously mixing all the components and measuring the resultant fusion temperature.

Consider successive additions. If the material at hand, before adding the i^{th} component, is treated as a homogeneous pure component, the fusion temperature according to the first approach can be predicted from:

$$\frac{1}{T_i} = \frac{1}{T_{i-1}} + \frac{R}{\Delta H_{i-1}} \ln (1-x_i) \quad (10-3)$$

where T_{i-1} and T_i are the fusion temperatures before and after adding the i^{th} component, x_i is the mole fraction of the i^{th} component, and ΔH_{i-1} is the hypothetical enthalpy of fusion of the mixture (treated as though it were a pure component). Note that x_i has to be calculated based on the components present at that instant in the mix, i.e.,

$$x_i = \frac{n_i}{\sum_{j=1}^i n_j} \quad (10-4)$$

where n_i is the number of moles of the i^{th} component in the system. Therefore, ΔH_{i-1} is not a true property of the $(i-1)^{\text{th}}$ component since it depends on the order of mixing and the composition of the mixture.

The second approach to describe the melting point of a mixture can be formulated mathematically if it is assumed that all the perturbing components are mixed simultaneously, that each perturbing component is dilute, and that the influence of other components on the properties of one particular component is small. Thus:

$$\frac{1}{T} = \frac{1}{T_o} + \sum_{i=1}^N \frac{R}{\Delta H_o} \ln (1-x_i) \quad (10-5)$$

and

$$x_i = \frac{n_i}{N+1 + \sum_{j=1}^N n_j} \quad (10-6)$$

where the subscript 'o' refers to the base component and N is the number of perturbing components.

The first approach could be implemented to coal ash if the values of ΔH_i were known, if the mixtures were dilute, and if no phase changes occur. However, not all the components of coal ash are dilute, phase changes do occur, and the concentration dependence of ΔH_i is not known.

The second approach is therefore not useful as such for coal ash because ash is not a dilute mixture of different components and its behavior is not that of an ideal solution.

In order to overcome these difficulties and to obtain a practical model, the two approaches were combined and a new model was created based on the following assumptions: 1) an "average" coal ash composition exists which can be treated as a pseudo pure-component; 2) small composition perturbations around the average ash composition create small perturbations and do not result in new phases; 3) the concentration perturbations around the average compositions are small enough that the solutions behave like ideal ones; 4) each component is considered as a perturbing component. Rigorous mathematical formulation of this model is:

$$\frac{1}{T} = \frac{1}{T_0} + \sum_{i=1}^N \frac{R}{\Delta H_0} \ln (1-\Delta x_i) \quad (10-7)$$

where T_0 and ΔH_0 refer to the average ash properties and Δx_i is the deviation of the mole fraction of the i^{th} component from that of the average mole fraction of the i^{th} component, and N is the total number of components. Correlations of T vs. Δx_i were greatly improved when the value of ΔH_0 was allowed to float, i.e., the correlation used:

$$\frac{1}{T} = \frac{1}{T_0} + \sum_{i=1}^N \frac{R}{A_i} \ln (1-\Delta x_i) \quad (10-8)$$

A_i is used to replace what would be an ill-used ΔH_i . Equation (10-8) is not truly rigorous in the thermodynamic sense but it gave the best correlation of the available empirical data. Each ash composition and an average ash composition were calculated from the available data set. The T_0 and A_i were calculated empirically to obtain the correlation that minimized the residual sum of squares.

Ash is only approximately characterized in composition and in its fusion temperatures (2,5,6), and therefore it is doubtful that ash can be treated accurately. Therefore, the first-order thermodynamic approximation of equation (10-8) may be an acceptable treatment, since the floating A_i 's compensate for some of the uncertainties.

10.4 DATA

The major source of data for the correlation was Bureau of Mines Bulletin 567 "Analysis of Ash from United States Coal" (5), which includes data on a broad rank range (anthracite, bituminous, subbituminous and lignite) from a broad geographic range (25 states). More recent literature data have also been included. The sources are listed in Table 10.1.

The reported compositions include only the major constituents of the ash. Minor components such as Mn compounds, and often Na and K compounds, were not reported.

The theory requires mole fractions of components in the ash but the literature typically reported weight percents of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , Na_2O , K_2O , TiO_2 , SO_3 , and P_2O_5 . The data must be treated as follows:

- 1) Determine the moles of each oxide in the ash sample.
- 2) Calculate CaO , K_2O and MgO remaining after reaction with SO_3 and P_2O_5 .
- 3) Calculate the moles of FeO from the Fe_2O_3 .
- 4) Sum the moles of sulphates, phosphates, TiO_2 , Na_2O and K_2O , as 'others'.
- 5) Calculate the mole fraction of SiO_2 , Al_2O_3 , FeO , CaO , MgO , and 'others'.
- 6) Calculate reciprocal temperatures for the ASTM D-1857 fusion temperatures (IDT, ST, FT) expressed in absolute units.
- 7) Calculate $\bar{x}_i$ and the $\ln(1-\Delta x_i)$ where $\bar{x}_i$ is the average composition of the i^{th} component and Δx_i is the deviation of that component from the average.
- 8) If the objective is to find the best parameters that describe the data set, then multiple regression has to be done to determine the best A_i and T_0 that describe the data. However, if the objective is to predict the melting point, the values of Δx_i have to be plugged into the equation with the best-known values of A_i and T_0 .

TABLE 10.1
SOURCES OF ASH DATA

Number of Data Points Accepted	Test Method(s) Used	References
13	presumed ASTM D-1857 plus Mossbauer Spectroscopy	Bryers, R. W., and Taylor, T. E. (3)
8	ASTM D-1857	Huffman, G. P. Huggins, F. E., and Dynmyre, B. R. (6)
214	Various	Selvig, W. A., and Gibson, F. H. (5)
7	presumed ASTM	Hale, G. L., Levasseur, A. A., Tyler, A. L., and Hensel, R. P. (7)
3	presumed ASTM	Borio, R. W., Goetz, G. T., and Levasseur, A. A. (8)
18	ASTM	Borio, R. W., Narciso, R. R. (9)
TOTAL 263		

The statistical correlation was performed by the Statistical Analysis System (SAS) available at the Triangle Universities Computing System.

Two data integrity checks were performed to eliminate inconsistent data sets. Data were rejected where the combined SO_3 and P_2O_5 was stoichiometrically larger than the sum of CaO , Na_2O , and K_2O and MgO . Data sets were also rejected where the IDT, ST and FT were not in an increasing order.

Where the reported temperature was labeled "above some value," the data were discarded to eliminate "class" variables from the statistical analysis. Two hundred sixty-three (263) sets were accepted.

10.5 RESULTS

Of the 263 data sets that were accepted, 65 included the concentrations of all the 10 components. When only those 65 were used to determine the coefficients, and the term ' $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ' was allowed to be a seventh independent variable, it was found to be statistically insignificant ($\alpha = 0.9$ where α is the probability of a greater statistic occurring by chance alone). As a result, ' $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ' was eliminated as an independent variable and the mole fractions of Na_2O and K_2O were included in the 'other' term.

Table 10.2 lists the statistics, average composition and the individual A_i as determined by the linear correlation of reciprocal temperature vs. $\ln(1-\Delta x_i)$ for each of the 3 ASTM D-1857 fusion temperatures. For each temperature the model is highly significant ($\alpha < .001$). Also, each of the seven parameters is a highly significant ($\alpha < .001$) effect.

The large number of data, coupled with the high F-statistics (N and F in Tables 10.2 and 10.4), indicate that there is a strong relation between the reciprocal temperature and the $\ln(1-\Delta x_i)$ terms. The correlation coefficient (r^2 in Tables 10.2 and 10.4) indicates that about 70% of the variance in the data is accounted for by the 7-term model.

Figures 10.1, 10.2, and 10.3 illustrate the quality of the model predictions. The figures represent the predicted IDT, ST and FT from

TABLE 10.2
CORRELATION STATISTICS AND PARAMETER COEFFICIENTS
FROM THE COMPLETE DATA SET

ASTM D-1857 TEMPERATURE		IDT	ST	FT	95% UCL FT	95% LCL FT
Model Statistics	N	263	263	263	-	-
	F	98.	115.	87.	-	-
	R ²	0.70	0.73	0.67	-	-
	σ , °R*	125.	119.	114.	-	-
Model Coefficients	T ₀ , °R*	2539.	2661.	2846.	2863.	2828.
	A _{SiO₂} , BTU/lb-mole**	3153.	3548.	4474.	5196.	3928.
	A _{Al₂O₃} , BTU/lb-mole**	2065.	2054.	2726.	3037.	2472.
	A _{FeO} , BTU/lb-mole**	4648.	4949.	6219.	7324.	5403.
	A _{CaO} , BTU/lb-mole**	3494.	3869.	5304.	6219.	4623.
	A _{MgO} , BTU/lb-mole**	3282.	3927.	5218.	6535.	4343.
	A _{other} , BTU/lb-mole**	3137.	3349.	4749.	5540.	4156.
Average Mole Fractions						
Component	SiO ₂	Al ₂ O ₃	FeO	CaO	MgO	'Other'
$\bar{x}_i$	.51340	.16392	.16387	.05123	.03415	.07341

*Divide by 1.8 to convert to K.

**Multiply by 2324. to convert to J/Kmol.

TABLE 10.3

FIRST-ORDER EFFECT OF AN INDEPENDENT 0.05 MOLE FRACTION
INCREASE OF EACH COMPONENT ON THE ASTM D-1857
ASH FLUID TEMPERATURE

<u>COMPONENT</u>	<u>TEMPERATURE CHANGE¹</u>
SiO ₂	+ 196°R
Al ₂ O ₃	+ 339°R
FeO	+ 139°R
CaO	+ 165°R
MgO	+ 167°R
'Other'	+ 185°R

¹Divide by 1.8 to convert to K.

TABLE 10.4
CORRELATION STATISTICS AND PARAMETER COEFFICIENTS
USING 'LOW CaO' DATA ONLY

ASTM D-1857 TEMPERATURE	IDT	ST	FT	95% UCL FT	95% LCL FT	
Model Statistics						
N	222	222	222	-	-	
F	110.	167.	123.	-	-	
r ²	.75	.82	.78	-	-	
σ, °R*	117.	101.	97.	-	-	
Model Coefficients						
T ₀ , °R*	2570.	2698.	2896.	2914.	2879.	
A _{SiO₂} BTU/lb-mole**	2162.	2402.	3225.	4110.	2653.	
A _{Al₂O₃} BTU/lb-mole**	1608.	1657.	2287.	2713.	1977.	
A _{FeO} BTU/lb-mole**	2993.	3192.	4282.	5808.	3392.	
A _{CaO} BTU/lb-mole**	2496.	3151.	4496.	6704.	3383.	
A _{MgO} BTU/lb-mole**	2605.	2709.	3637.	4935.	2880.	
A _{'other'} BTU/lb-mole**	2482.	2717.	4219.	5694.	3351.	
Average Mole Fractions						
Component	SiO ₂	Al ₂ O ₃	FeO	CaO	MgO	'Other'
$\bar{x}_i$	.55721	.17694	.15784	.031647	.023509	.053839

*Divide by 1.8 to convert to K

**Multiply by 2324. to convert to J/Kmol

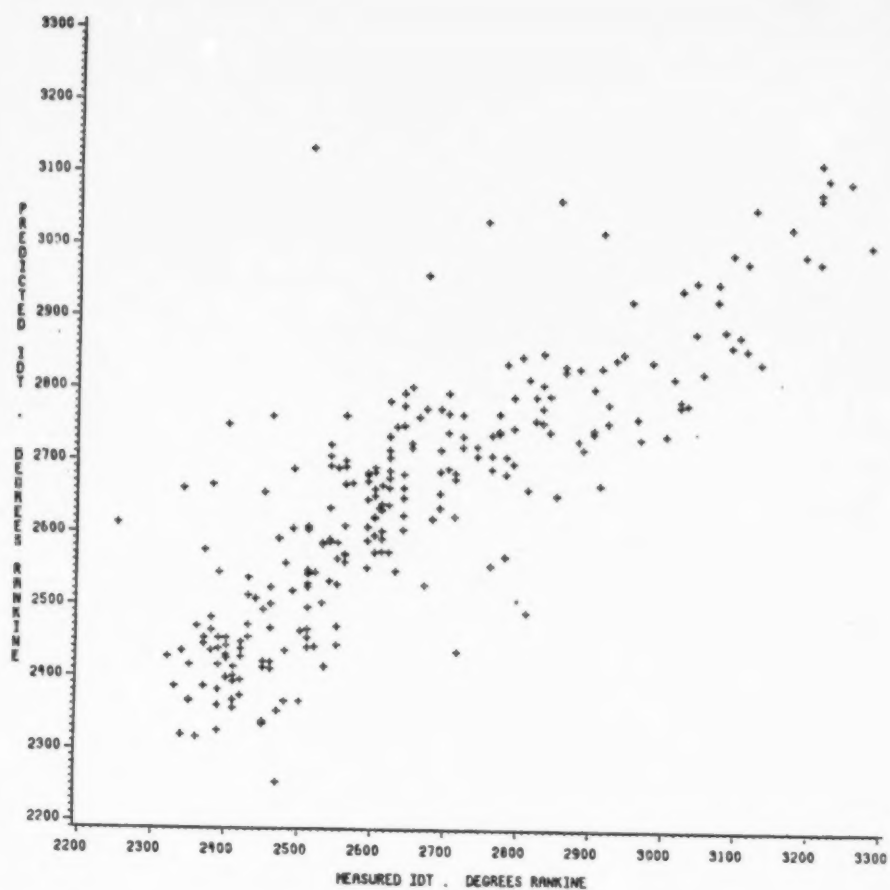


Figure 10.1 Initial deformation temperature (IDT) correlation

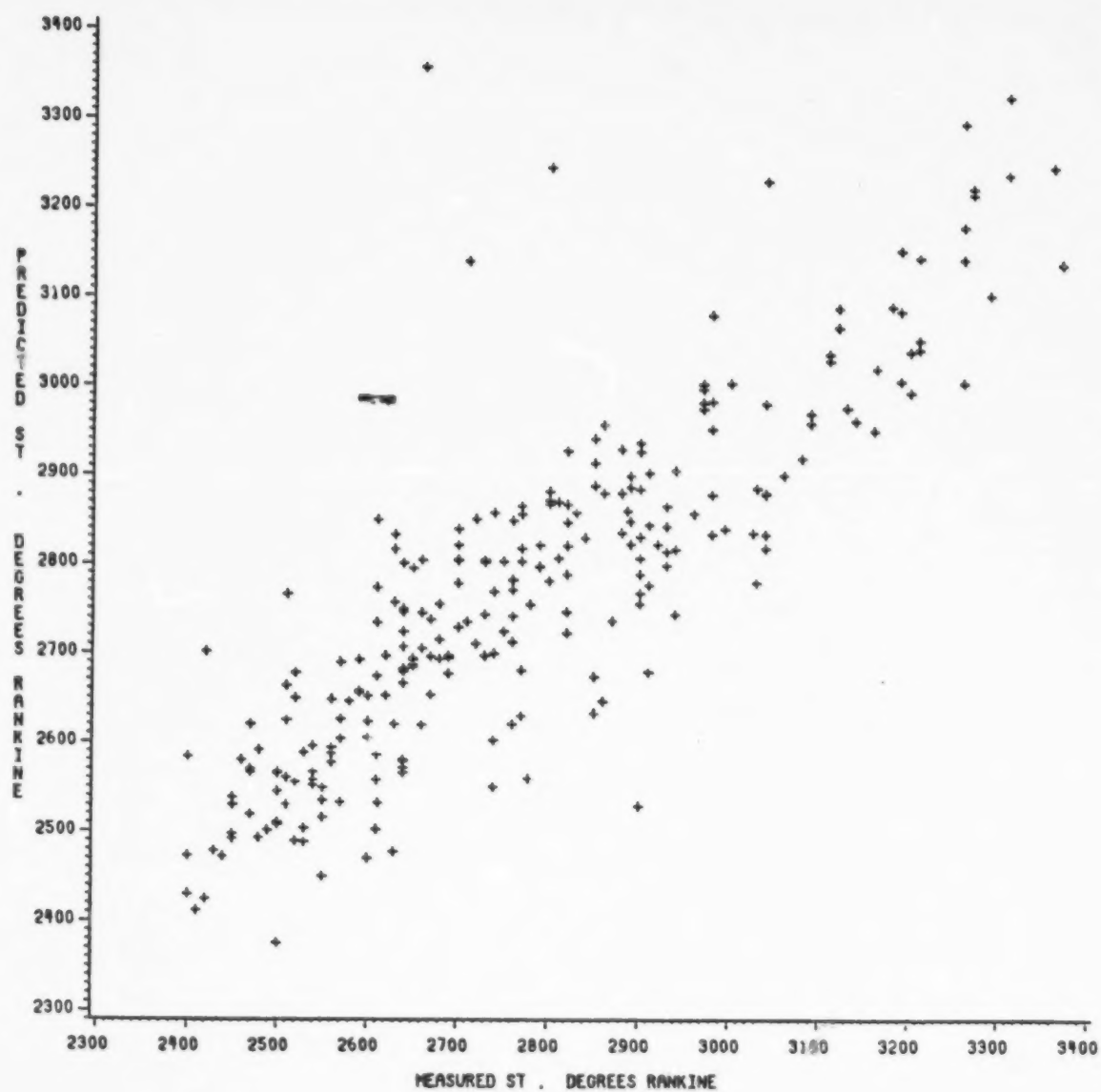


Figure 10.2 Softening temperature (ST) correlation results

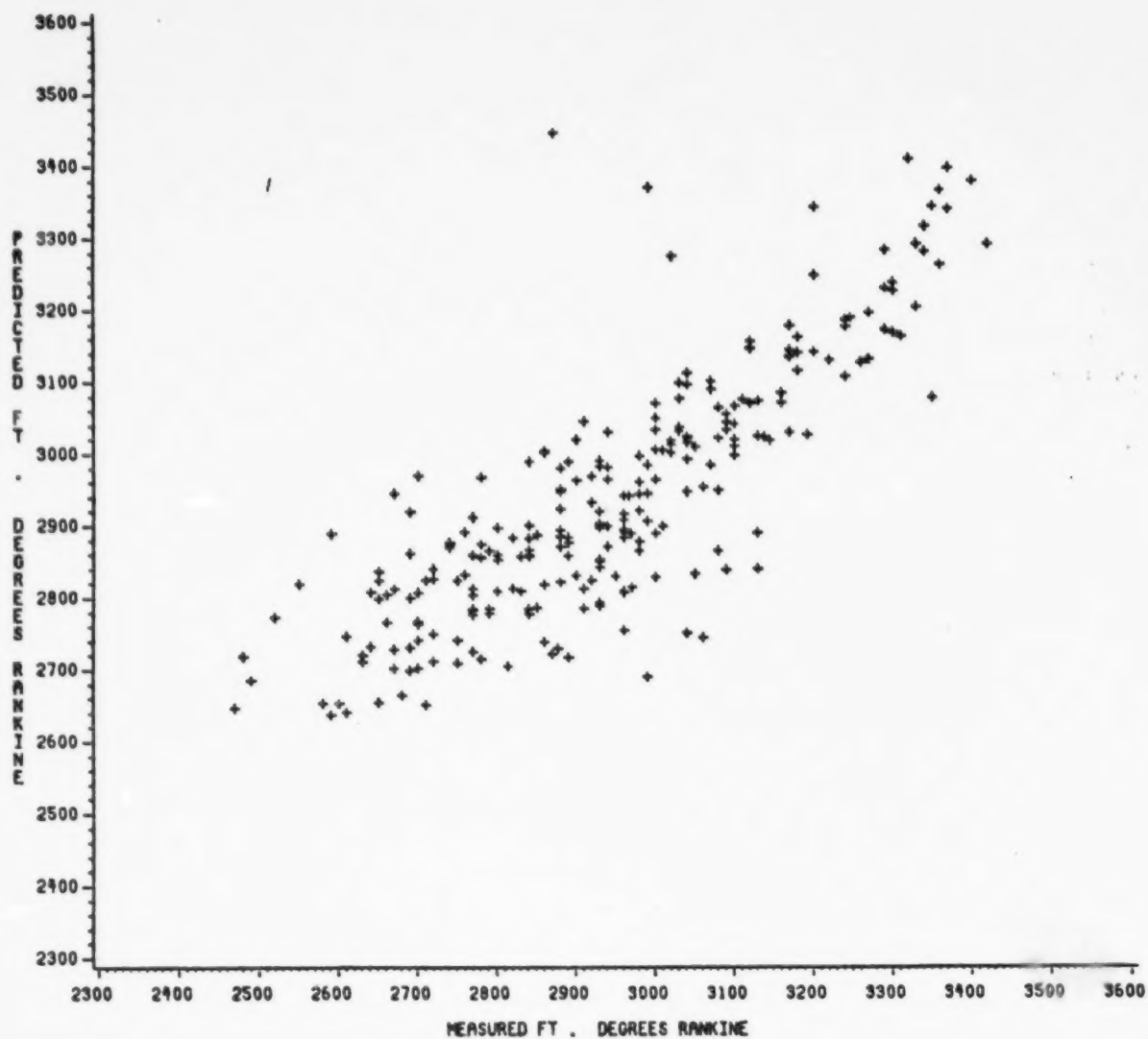


Figure 10.3 Fluid temperature (FT) correlation results

this model vs. the actual IDT, ST and FT reported in the literature for all 263 data. Note that the data cluster mainly within about 100°R (56°K) of the 1:1 diagonal. Ideally the data would fall on the 1:1 diagonal exactly.

10.6 DISCUSSION

The relatively small A_i associated with Al_2O_3 indicates that alumina can have the most significant influence on fusion temperatures. Table 10.3 indicates the change in predicted fluid temperature when the mole fraction of each component is increased independently by 0.05 from the average composition. Such an actual occurrence is impossible since at least one other component must change simultaneously, but the treatment generates a feel for the influence of each component on the temperature.

Approximately a 0.05-mole fraction increase in Al_2O_3 with an equivalent decrease in SiO_2 will cause about a 196°F (79°K) increase in the ash fluid temperature.

The standard error in predicted temperature ranged from 114 to 125°F (63 to 69°K). The ASTM D-1857 standard allows 100 to 150°F (56 to 83°K) intralab differences, which, by our implication, reflects a test standard deviation of 50 to 77°F (28 to 42°K). Again, by our interpretation, the ASTM D-2795 and D-1757 tests imply analytical composition variances that contribute a 50 to 150°F (28 to 83°K) to the standard deviation of the predicted temperature (depending on the composition and component covariance). A simple variance removal analysis indicates that there remains about a 0 to 90°F (0 to 50°K) standard error in the predicted temperature associated with other sources.

In comparison to Bryers and Taylor (3), this standard error is equivalent to their standard error determined by restricted coal classes. In comparison to Winegartner and Rhodes (2), the standard error here is higher, but the coal classes are not restricted here, there are nine fewer terms here, and each has a thermodynamic origin.

The thermodynamic model requires only 7 parameters of which 6 have an identical format, making it easy to use. The model works for a broad rank and geographic coal range.

Furnace experience (7,8,9) links alkalis with fouling but here they are found to have a negligible correlation to any of the three ash fusion temperatures. The main reason for this is that the alkalis are much more volatile than the other elements and consequently they concentrate on the tubes where the volatiles can condense. This phenomenon extenuates their impact on fouling without influencing much the total ash fusion temperature. A curious influence of the alkalis on fluid temperature was also experienced by Huggins et al. (10) who found that the ASTM fluid temperatures of K_2CO_3 -ash mixtures did not parallel the fluidus temperatures of ternary K_2O , Al_2O_3 , SiO_2 mixtures. (By comparison, the fluid temperatures of Fe_2O_3 and CaO additions to ash mimicked their respective ternary diagrams quite well.)

Perhaps the ASTM Ash Fusion Test does not treat the alkalis in such a manner that expresses their role in fouling. Effects such as vaporization depletion, early melt trickle down depletion, or complexing need to be included to define their role more accurately.

A significant improvement in the model prediction was noted when data from high CaO ash was excluded. Huggins et al. (9) show, in both ternary $SiO_2/Al_2O_3/CaO$ systems and artificial ash perturbed with CaO that, as the CaO is increased, the fluidus temperature decreases until there is sufficient CaO to induce new phases. Subsequent increases in CaO cause the fluidus temperature to rise. Applying their indications that the other minerals in the ash displace the inflection point by about 3.0 weight percent CaO in the ternary diagram, 41 'high CaO ' (based on both the SiO_2 and Al_2O_3 contents) samples were excluded from the original 263 data. Two hundred twenty-two (222) data sets remained. The freezing point depression equation (10-1) is not valid across eutectic boundaries and the correlative ability should be enhanced with the restricted data. Indeed, as the statistics in Table 10.4 show,

the predictive ability within the 'low CaO' data is improved significantly ($\alpha < .05$) over the nonrestricted data in Table 10.2.

Figures 10.4, 10.5 and 10.6 graph the predicted IDT, ST, and FT vs. the measured IDT, ST, FT for the 222 'low CaO' data. A visual comparison to Figures 10.1, 10.2, and 10.3 confirms the reduced scatter and hence the correlation improvement when considering 'low CaO' only.

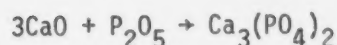
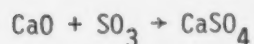
The complementary high CaO data (not shown) produced correlations with some high degree of uncertainty. This could possibly be the result of either too few linearly independent sets in the 41 data sets, or remaining eutectic crossings due to the very high CaO sets and the multitude of available phases.

10.7 AN EXAMPLE CALCULATION

Objective: Predict the Initial Deformation Temperature of an ash using English engineering units.

Method: The composition is listed in line 2 of Table 10.5. First convert the weight percents to lb-moles per 100 lb of ash by dividing the weight percents of each oxide by the respective molecular weight. The molecular weights are listed in line 3 and the lb-moles/100 lb ash basis are in line 4. Under reducing conditions the Fe_2O_3 reported will be in the FeO form. Line 5 shows the composition change, and line 6 the doubled moles of FeO.

According to the reactions



for each mole of SO_3 in the ash one mole of CaO is actually converted to CaSO_4 . Similarly for each P_2O_5 mole, 3 moles of CaO exist as one mole of $\text{Ca}_3(\text{PO}_4)_2$. The moles of CaSO_4 and $\text{Ca}_3(\text{PO}_4)_2$ were calculated and are shown included in the 'other' term on line 8. Note that the moles of CaO, SO_3 and P_2O_5 have been reduced appropriately. If some

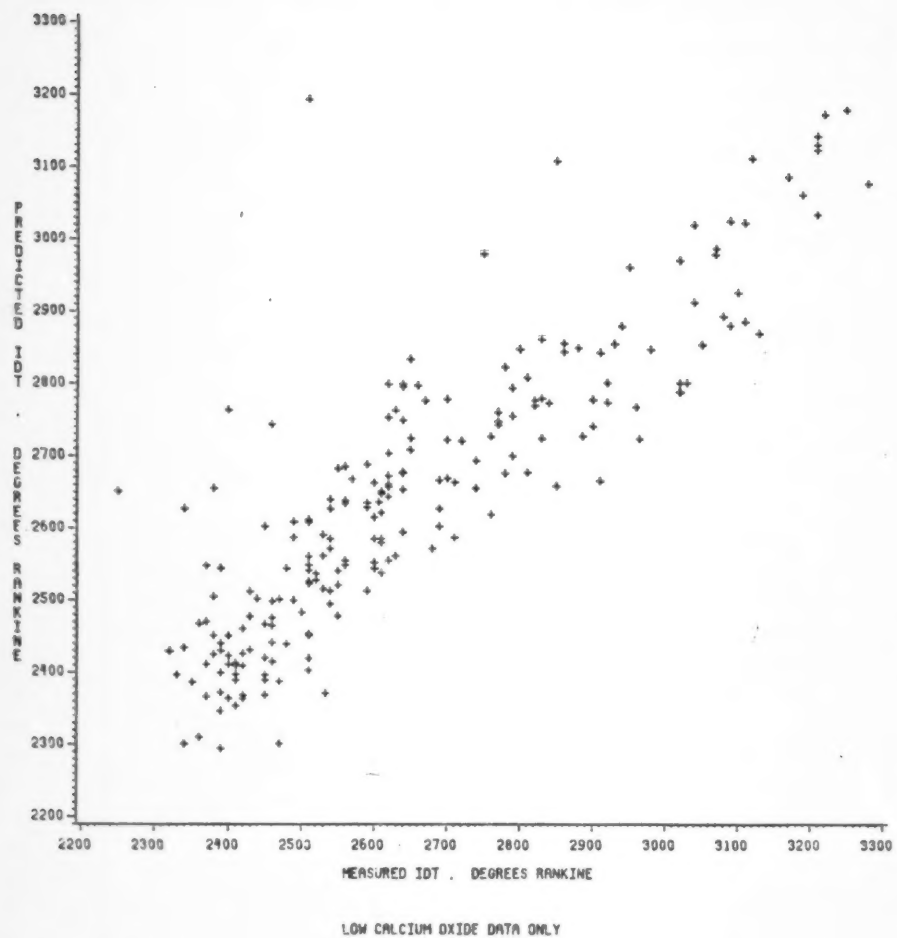


Figure 10.4 Initial deformation temperature (IDT) correlation

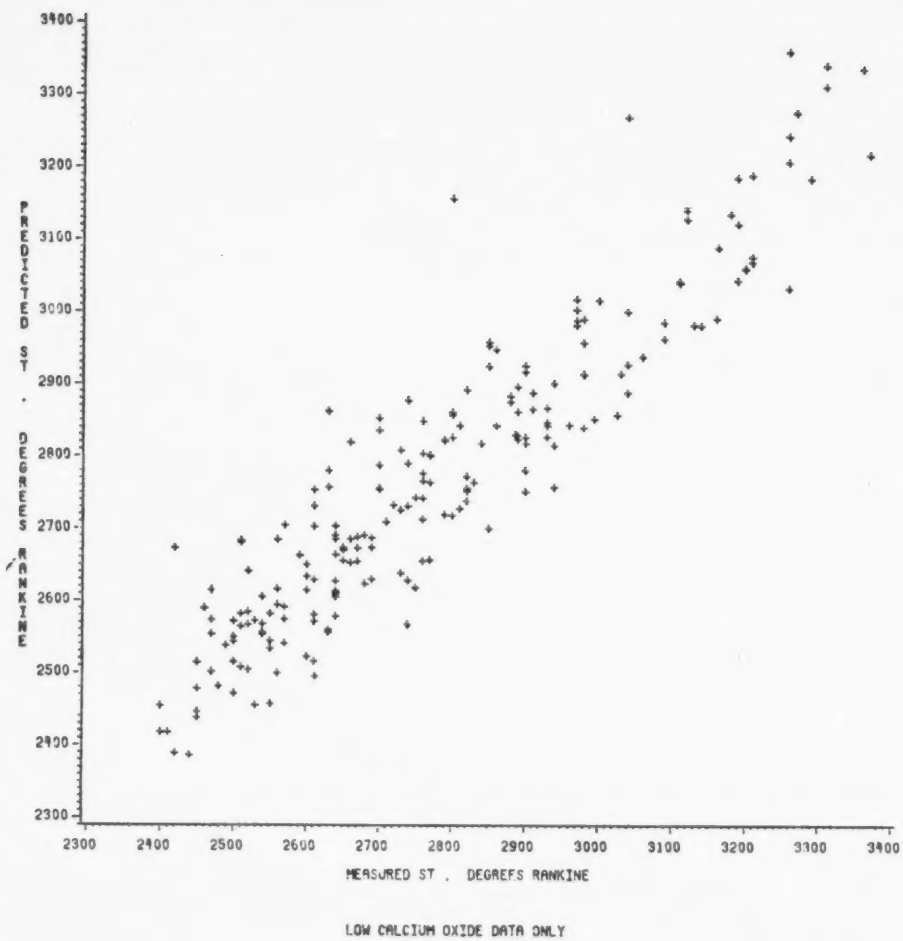
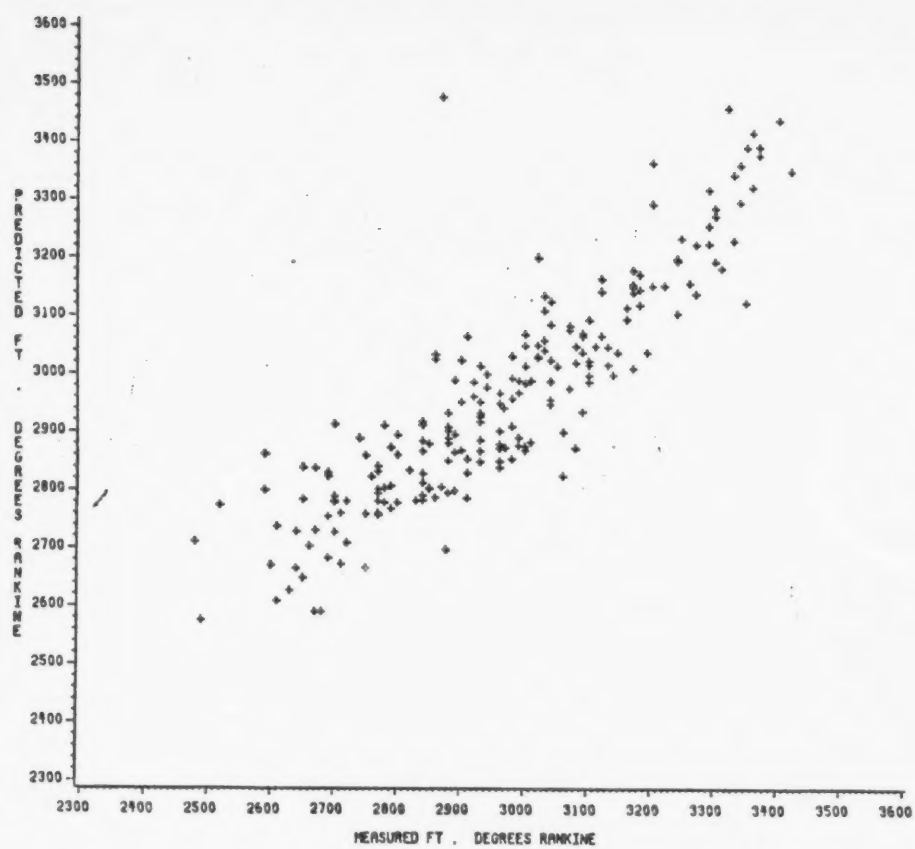


Figure 10.5 Softening temperature (ST) correlation results



LOW CALCIUM OXIDE DATA ONLY

Figure 10.6 Fluid temperature (FT) correlation results

TABLE 10.5
EXAMPLE INITIAL DEFORMATION TEMPERATURE PREDICTION

LINE #	DESCRIPTION	VALUES										
1	Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₃	P ₂ O ₅	
2	Wt % Ash	48.0	26.1	10.3	6.1	0.7	1.0	1.0	1.3	4.8	0.5	
3	Molecular Weight	60.09	101.96	159.69	56.08	40.30	61.98	94.20	79.90	80.96	141.95	
4	lb moles/100 lb ash	.7988	.2560	.0645	.1088	.0174	.0161	.0106	.0163	.0593	.0035	
5	Composition changed			FeO								
6	lb moles changed			.1290								
7	Composition changed								OTHER			
8	lb moles changed				.0389				.0791	.0000	.0000	
9	Composition Status	SiO ₂	Al ₂ O ₃	FeO	CaO	MgO	'other'	Sum				
10	lb mole/100 lbs	.7988	.2560	.1290	.0389	.0174	.1058	1.3459				
11	mole fractions	.5935	.1902	.0958	.0289	.0129	.0786	NA				
12	$\bar{x}_i$ from Table 4	.5572	.1769	.1578	.0317	.0235	.0538	NA				
13	Δx_i	.0363	.0133	-.0620	-.0028	-.0106	.0248	NA				
14	$R/A_i \times 10^3(^{\circ}R)^{-1}$	.9192	1.2358	.6640	.7962	.7628	.7990	NA				
15	$R/A_i \ln(1-x_i) \times 10^6(^{\circ}R)^{-1}$	-33.99	-16.55	33.94	2.23	8.04	-20.07	-26.40				

SO_3 and P_2O_5 remain, deplete the Na_2O then K_2O then MgO by the appropriate stoichiometric equations and add the salts to the 'other' class.

Add the remaining moles of Na_2O and K_2O to the 'other' class and delete Na_2O , K_2O , SO_3 and P_2O_5 from the composition list. This action is shown on lines 9 and 10 of Table 10.5.

Sum the six lb-mole/100 lb of ash values on line 10 to give the total number of lb-moles/100 lb of ash and then divide each of the six by the sum to give the mole fractions of each component as shown on line 11.

This example is a low calcium ash; therefore, use Table 10.4 to find the equation coefficients. The average mole fractions from Table 10.4 are reproduced on line 12 of Table 10.5 and the perturbation to the average ash (line 12-line 11) is shown on line 13. The A_i from Table 10.4 have been divided into the gas law constant ($R = 1.9872$ BTU/lb-mole- $^{\circ}\text{R}$) and listed on line 14 of Table 10.5

Line 15 contains the values of $(R/A_i) \cdot (\ln(1-\Delta x_i))$. The sum of line 15 is -0.00002640 ($^{\circ}\text{R}$) $^{-1}$. The reference temperature from Table 10.4 is 25070°R and its reciprocal is 0.000389 lb ($^{\circ}\text{R}$) $^{-1}$. The reciprocal of the Initial Deformation Temperature is the sum of the two reciprocal temperatures ($+0.00036271$) and the IDT is therefore 2757°R or 2297°F . By comparison, the reported IDT was 2260°F .

The calculation can be performed by a programmable calculator. A basic program which performs the calculations is available from Dr. Attar.

10.8 CONCLUSION

A seven-parameter equation, grounded in thermodynamics, predicts ash fusion temperatures with a standard deviation of 114 to 125°F (63 to 69°K) within the data base upon which it was correlated. The equation is equivalently powerful to previous but more complex formulae. Although not fully rigorous here, the thermodynamic approach is a theoretical improvement and should be the basis of future work.

Possible improvements may exist in appropriately accounting for the nonanalyzed portion of the ash, and in defining separate coefficient sets for several classes of coals to better account for compositions that cross eutectic boundaries on the temperature versus composition 'surface'. Further, preliminary thermodynamic considerations of an 'activity' coefficient have shown some improvement in the correlational ability.

ACKNOWLEDGEMENTS

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10.10 NOMENCLATURE

- A_i = parameter to replace what would have been an ill-used ΔH_i , BTU/lbmole or J/mol
 F = mean sum of squared deviations of the model divided by the residual mean sum of squared deviations, a statistic that indicates how well the model accounts for the dependent variable
 T = one of the three ASTM D-1857 Fluid Temperatures, °R or K
 IDT = ASTM D-1857 Initial Deformation Temperature, °F or K
 N = number of data points, number of components
 n_i = number of moles of the i^{th} component
 R = gas law constant, 1.9872 BTU/lbmole/°F or 8326.4 J/Kmol-K
 r^2 = the sum of squared deviations accounted for by the model divided by the total sum of squares, a statistic that indicates the fraction of dependent variable variation that is accounted for by the model
 ST = ASTM D-1857 Softening Temperature, °F or K
 x_i = mole fraction of the i^{th} component
 $\bar{x}_i$ = average mole fraction of i
 α = the probability of a greater statistic occurring by chance alone
 ΔH = heat of fusion of the pure substance, BTU/lbmole or J/Kmol
 Δx_i = $x_i - \bar{x}_i$
 σ = standard error. The standard deviation of the difference between the predicted and reported temperature, a combined measure of the model predictive precision and analytical data precision, °R or K.

Subscript o = for the base substance

CHAPTER 11

MEASUREMENT OF DIFFUSION AND ADSORPTION CHARACTERISTICS IN FRESH AND FOULED HDS CATALYSTS

11.1 INTRODUCTION

The determination of adsorption and diffusion parameters from residence time distribution curves using the dynamic pulse dispersion method has been considered by numerous investigators (1-17). Much of this work has focused on measuring diffusion and adsorption in spherical pellets of molecular sieves which have relatively small and uniform pores. In general, a model is proposed which describes the functional dependence of pulse dispersion in terms of specific process coefficients. Experimentally measured dispersion characteristics can then be directly attributed to the process coefficients by application of the proposed model.

The pore structure and surface activity of a porous solid are intimately connected to the dispersion behavior of an adsorbable tracer. In this sense, the pulse dispersion technique provides a powerful method for probing the physical and chemical attributes of a porous solid which is packed in a column or reactor.

A number of important process operations require the use of porous solids as either reactants or catalysts. Common to many of these operations is the time-dependent variation of pore structure and surface activity during processing. Such is the case with HDS catalysts used in coal liquefaction or coal liquids upgrading. The progress of reaction in these heterogeneous solids results in the steady accumulation of deposited metals and carbonaceous matter. Striking reductions in the performance of these catalysts have been reported as a result of the fouling phenomena (18-19).

Conventional pore structure measurement techniques such as mercury penetration and inert gas adsorption porosimetry have helped understanding

the progress of fouling in HDS catalysts. However, these static pore structure analysis techniques suffer from the following shortcomings: 1) They cannot be applied in situ; 2) the conditions of the tests are far removed from the reaction conditions, 3) they provide an indirect interpretation of the primary phenomena of concern, that is, the dynamic behavior of reactants as they penetrate through the porous network. The pulse dispersion technique may provide a useful counterpart to conventional porosimetry in studying fouling by providing dynamic information relevant to diffusion and adsorption characteristics.

A few examples of the application of pulse dispersion to study the relation between pore structure transformations and diffusivity are found in the literature. Butt et al. used pulse dispersion to study the effects of coking on the transport properties of H-Mordenite (20). Debelack et al. measured diffusivities in coal as a function of the extent of gasification (21). Chou and Hegedus measured diffusivities in a catalyst containing a well-defined fouled zone (22).

This work considers the use of the pulse dispersion technique to study adsorption and diffusion in fresh and fouled HDS catalysts. Three sets of fresh and fouled catalysts have been obtained from the U.S. Department of Energy which undertook a study concerning the performance characteristics of various catalysts during coal liquefaction and coal liquid upgrading runs. The process conditions and performance of these catalysts have been reported elsewhere (18-19).

The catalysts studied in this work include a bimodal, Ni-Mo/ Al_2O_3 catalyst (RET 50570; an in-house DOE developmental catalyst), a unimodal Ni-Mo/ Al_2O_3 catalyst (Shell 324 modified), and a bimodal Co-Mo/ Al_2O_3 catalyst (Amocat 1A). Fresh (unsulphided) and fouled catalysts of each type were packed in columns and the diffusion and adsorption characteristics of Ar, He, N_2 , Kr and CO_2 were studied in isothermal runs.

A model is developed which describes dispersion in cylindrical extrudite pellets possessing heterogeneous surface sites. The model is an extended version of the well-known Kubin-Kucera theory of linear chromatography (23). Gangwall et al. (8) give expressions for the Fourier

coefficients based on the Kubin-Kucera spherical pellet model. This work reports the functional expressions for the Fourier coefficients based on the cylindrical pellet with heterogeneous adsorption sites.

11.2 THEORY

A model is described for dispersion of an adsorbable tracer in a packed column containing porous cylindrical pellets. In the general case, a dual mode adsorption mechanism is considered in order to account for the heterogeneous nature of the surface.

The concentration $C(z,t)$ of an adsorbable tracer as a function of time and axial position in the column is obtained from the solution of the following material balance equations.

The mass balance for the tracer in the inter-pellet volume is given by:

$$\frac{D_a}{E} \frac{\partial^2 C}{\partial z^2} - \frac{V \partial C}{\partial z} - \frac{\partial C}{\partial t} - \frac{2D_e(1-E)}{RE} \left[\frac{\partial C_i}{\partial r} \right]_{r=R} = 0 \quad (11-1)$$

The mass balance for the tracer in the intra-pellet pore volume is given by:

$$\frac{D_e}{\beta} \frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial t} - \frac{\partial C_i}{\partial t} - \frac{\rho_p}{\beta} \left[\frac{\partial C_{a1}}{\partial t} + \frac{\partial C_{a2}}{\partial t} \right] = 0 \quad (11-2)$$

The rate of adsorption is assumed to be linear for both adsorption sites:

$$\frac{\partial C_{a1}}{\partial t} = K_{a1} (C_i - C_{a1}/K_{a1}) \quad (11-3)$$

$$\frac{\partial C_{a2}}{\partial t} = K_{a2} (C_i - C_{a2}/K_{a2}) \quad (11-4)$$

The external diffusion boundary condition is described by:

$$D_e \left[\frac{\partial C_i}{\partial r} \right]_{r=R} = k_f (C - (C_i)_{r=R}) \quad (11-5)$$

The internal diffusion boundary condition is given as:

$$\frac{\partial C_i}{\partial r} = 0 \quad \text{at } r = 0, t > 0 \quad (11-6)$$

An impulse function is assumed for the inlet pulse:

$$C = \delta(t) \quad \text{at } z = 0, t = 0 \quad (11-7)$$

The initial conditions are:

$$C = C_i = C_{a1} = C_{a2} \quad \text{at } z = 0, t = 0 \quad (11-8)$$

$C(z,t)$ is assumed to be bounded.

The Fourier transformed solution, $\bar{C}(iw)$, at $z = L$, is given by:

$$\bar{C}(iw) = \exp \left(P - \left(P^2 + \frac{iwEL}{D_a} (1 + h(iw)) \right)^{1/2} \right) \quad (11-9)$$

where, $w = n\pi/T$

$$P = VEL/2D_a \quad (11-10)$$

$$h(iw) = S_v k_f (1/iw - I_0(\sqrt{\lambda} R) / (-\frac{iwD}{k_f} \sqrt{\lambda} I_1(\sqrt{\lambda} R) - iwI_0(\sqrt{\lambda} R))) \quad (11-11)$$

$$S_v = 2(1-E)/RE \quad (11-12)$$

$$\lambda = \frac{iw\beta}{D_e} \left(1 + \frac{\rho_p}{\beta} (k_{a1} + k_{a2}) / (iw + k_{a1}/K_{a1} + k_{a2}/K_{a2}) \right) \quad (11-13)$$

11.3 MOMENT METHOD

A commonly used method for describing the functional dependence of the residence time distribution of a pulse on the process parameters is through moments. A straightforward extension of the results of Schneider and Smith (1) reveals expression for the first absolute and second central moments of the output pulse:

$$\mu_1' = (1/V)(1 + \delta_0) \quad (11-14)$$

$$\mu_2 = (2L/V)(\delta_1 + (D_a/E)(1 + \delta_0)^2/V^2) \quad (11-15)$$

where,

$$\delta_0 = ((1-E) \beta/E)(1 + (\rho_p/\beta)(K_{a1} + K_{a2})) \quad (11-16)$$

$$\begin{aligned} \delta_1 = & ((1-E) \beta/E)((\rho_p/\beta)(K_{a1}^2/k_{a1} + K_{a2}^2/k_{a2}) \\ & + (R^2\beta^2/8)(1+(\rho_p/\beta)(K_{a1}+K_{a2}))^2(1/D_e+4/k_fR)) \end{aligned} \quad (11-17)$$

and the moments are defined as:

$$\mu_2 = \int_0^\infty (t - \mu_1')^2 C(L,t) dt / \int_0^\infty C(L,t) dt \quad (11-18)$$

$$\mu_1' = \int_0^\infty t C(L,t) dt / \int_0^\infty C(L,t) dt \quad (11-19)$$

11.4 FOURIER ANALYSIS

The real and imaginary parts of Fourier solution, $\bar{C}(iw)$, in equation (11-9) are separated (Appendix). The Model Fourier coefficients (b_n, a_n) are given by $1/T$ times the real and imaginary parts, respectively. The experimental Fourier coefficients (b_n^*, a_n^*) are calculated from the normalized experimental pulse, $C^*(t)$, as follows:

$$b_n^* = 1/T \int_0^{2T} C^*(t) \cos(n\pi t/T) dt \quad (11-20)$$

$$a_n^* = 1/T \int_0^{2T} C^*(t) \sin(n\pi t/T) dt \quad (11-21)$$

$$b_0^* = 1/2T \quad (11-22)$$

where T is sufficiently large to allow complete elution of the pulse tail. Utilizing a methodology similar to that of Gangwall et al., the process coefficients are fitted by minimizing the variance of an objective function, F , defined as

$$F = \sum_{n=1}^M (A_n - A_n^*)^2 \quad (11-23)$$

where,

$$A_n = T(a_n^2 + b_n^2)^{1/2} \quad (11-24)$$

$$A_n^* = T(a_n^{*2} + b_n^{*2})^{1/2} \quad (11-25)$$

11.5 EXPERIMENTAL PROCEDURE

A schematic of the apparatus is provided in Figure 11.1. The flow of carrier gas (CG1) through the column is regulated by needle valve, NV1. The flow of carrier gas is measured by a soap bubble meter. Flow rates are checked before and after each pulse. Column head pressure is monitored at P1. The pressure drop through the column was typically less than 1 psi for most runs. An independent stream of carrier gas (CG2) is mixed with tracer gas (TG) through flow meters F1 and F2. The resulting mixture (5-10% tracer, 1 ATM) is directed through a 8-port injection valve with a 50 μ L sample loop. The column is contained in a forced-air oven. The injector and detectors are independently heated. Digital temperature readout is provided for each temperature-controlled component. The output pulses are monitored by a thermal conductivity detector at T1. The analog TCD signal is converted to digital form at AD1 under computer direction, C1. The digital data are stored in the computer workspace (Digital Corporation, MINC II) for further processing and on diskette for permanent record. The frequency of digitization is varied in order to define the output pulse by a minimum of approximately 100 points.

The extra column volume (dead space) is calibrated from blank runs using an empty column of known volume. The extra column volume is calculated to be less than 6% of the total system volume. Corrections of extra column effects are made for first-moment calculations only.

The columns are U-shaped single smooth 1/4" glass tubing 48 cm in length. Glass tubing is used to allow visual inspection of the packing characteristics of the extrudite pellets. The volume of each column is determined by volume filling with methanol. The columns are heated in flowing helium for one hour at 250°C to remove traces of methanol. The columns are connected directly to the transfer lines through stainless steel fittings with Teflon ferrules.

Each of the HDS catalysts considered in this study are extrudites of well-defined dimensions. Typical length-to-radius ratios for the

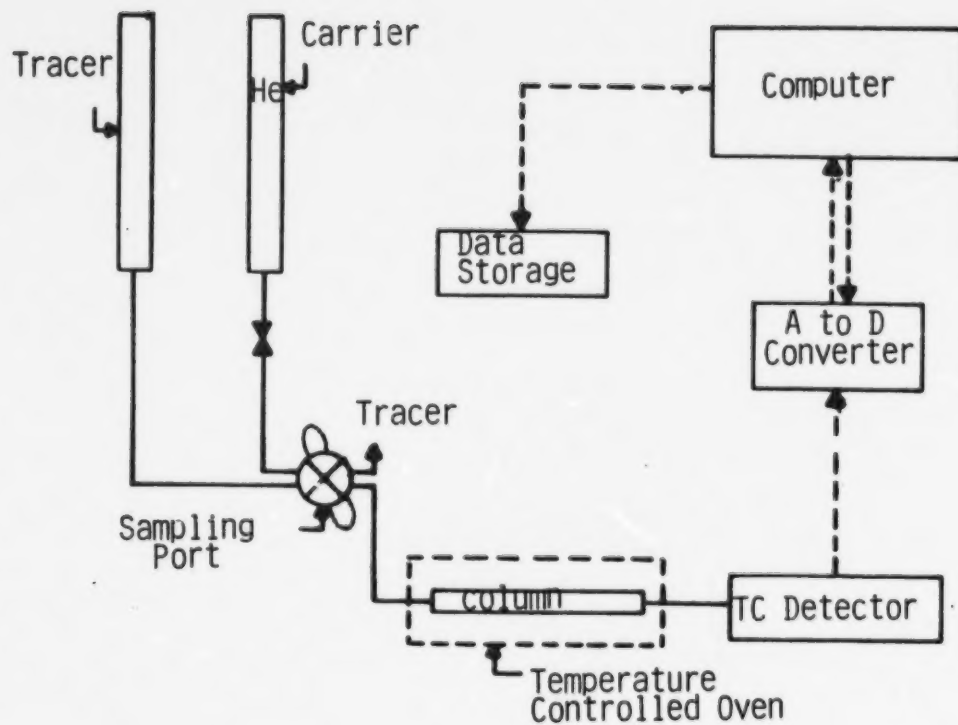


Figure 11.1 Schematic diagram of experimental apparatus used for measuring pulse dispersion

pellets are in the range of 10:1. Six pre-formed columns are packed with fresh and fouled HDS catalyst counterparts. The composition and characteristics of the catalysts are described in Table 11.1.

TABLE 11.1 COMPOSITION AND CHARACTERISTICS OF HDS CATALYSTS

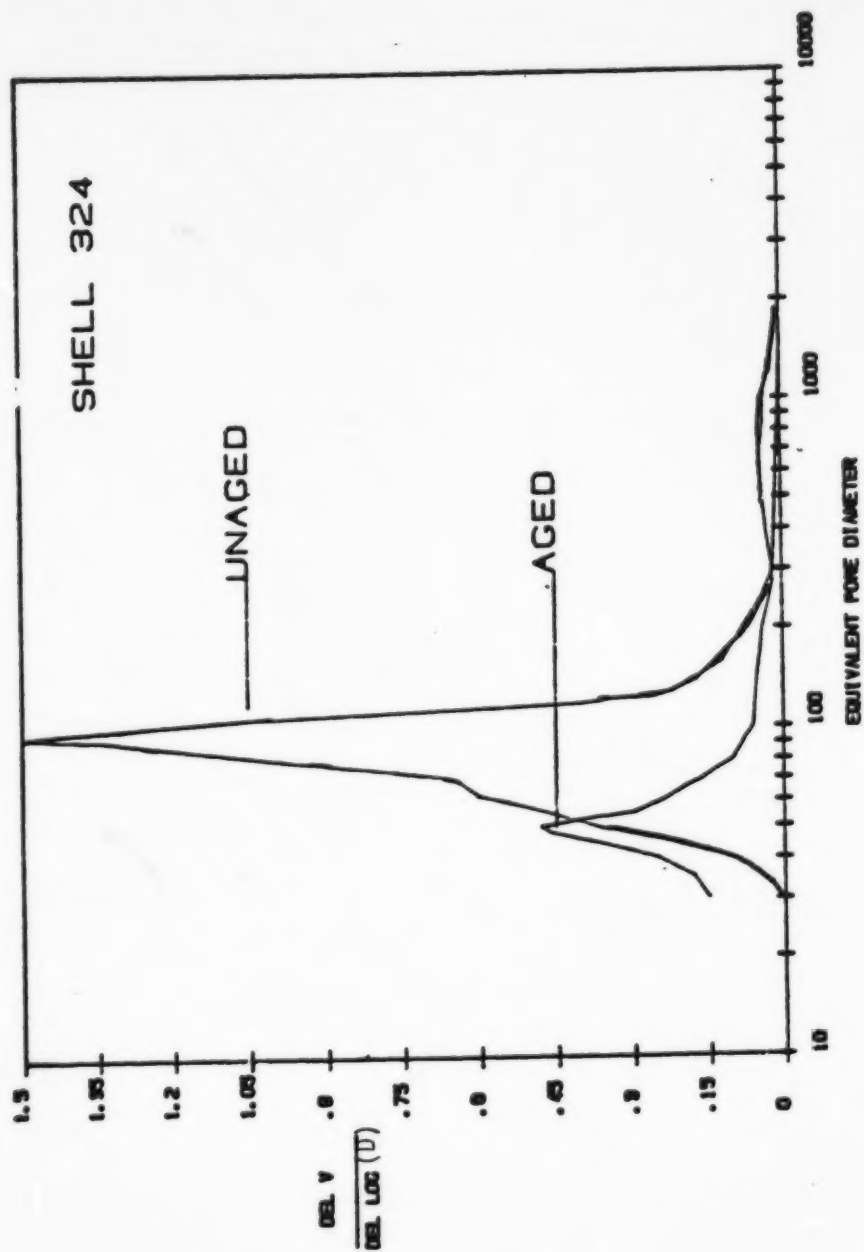
Type	Composition	Service
RET 59569	5.0 NiO, 29.0 MoO ₃ 66.0 Al ₂ O ₃	coal liquid upgrading (120 hr)
SHELL 324 m	3.24 NiO, 20.1 MoO ₃ 65.09 Al ₂ O ₃ , 6.87 P ₂ O ₅	coal liquid upgrading (120 hr)
AMOCAT 1A	3.0 CoO, 15.0 MoO ₃ 83.0 Al ₂ O ₃	coal liquefaction (100 hr)

BET and mercury penetration porosimetry data have been provided by the Department of Energy for each fresh and fouled catalyst. The pore structure information is summarized in Table 11.2. Graphs of the pore volume distributions are shown in Figures 11.2 to 11.4.

TABLE 11.2 SURFACE AREA AND PORE STRUCTURE OF THE HDS CATALYSTS

Type	Distribution	Apparent Density	Porosity	Surface Area
		g/cc		m ² /g
Fresh				
RET 50570	bimodal	1.033	.710	177
AMOCAT 1A	bimodal	1.077	.717	198
SHELL 324 m	unimodal	1.51	.600	188
fouled				
RET 50570	bimodal	1.420	.510	88
AMOCAT 1A	bimodal	1.429	.527	144
SHELL 324 m	unimodal	1.510	.25 ⁽¹⁾	96

¹⁾ By rough calculation, approximately 20% of the fouled Shell pore volume remains undetected by the mercury penetration procedure.



PORE SIZE DISTRIBUTION FOR AGED AND UNAGED CATALYST

Figure 11.2 Transcribed - DOE pore structure data

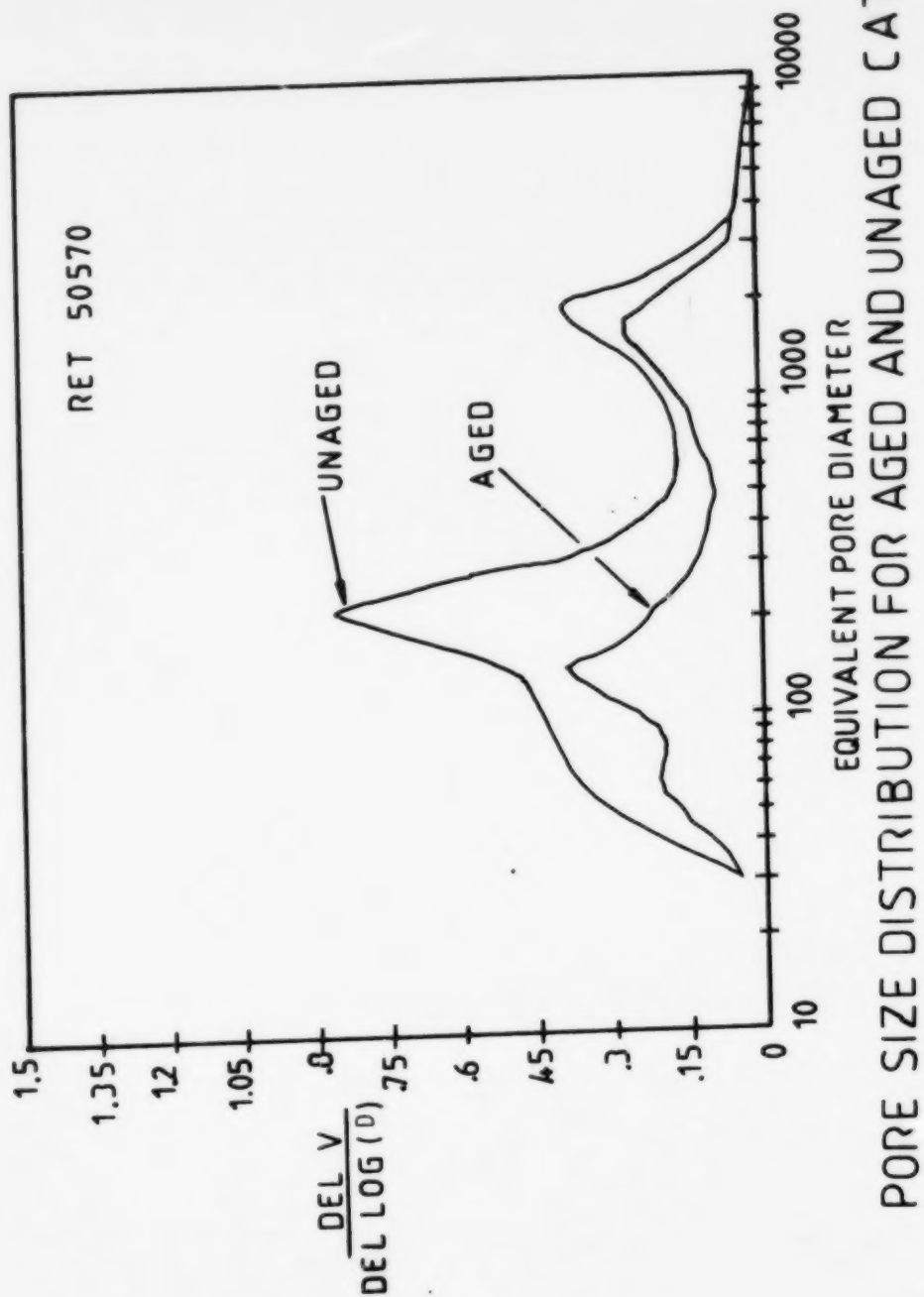
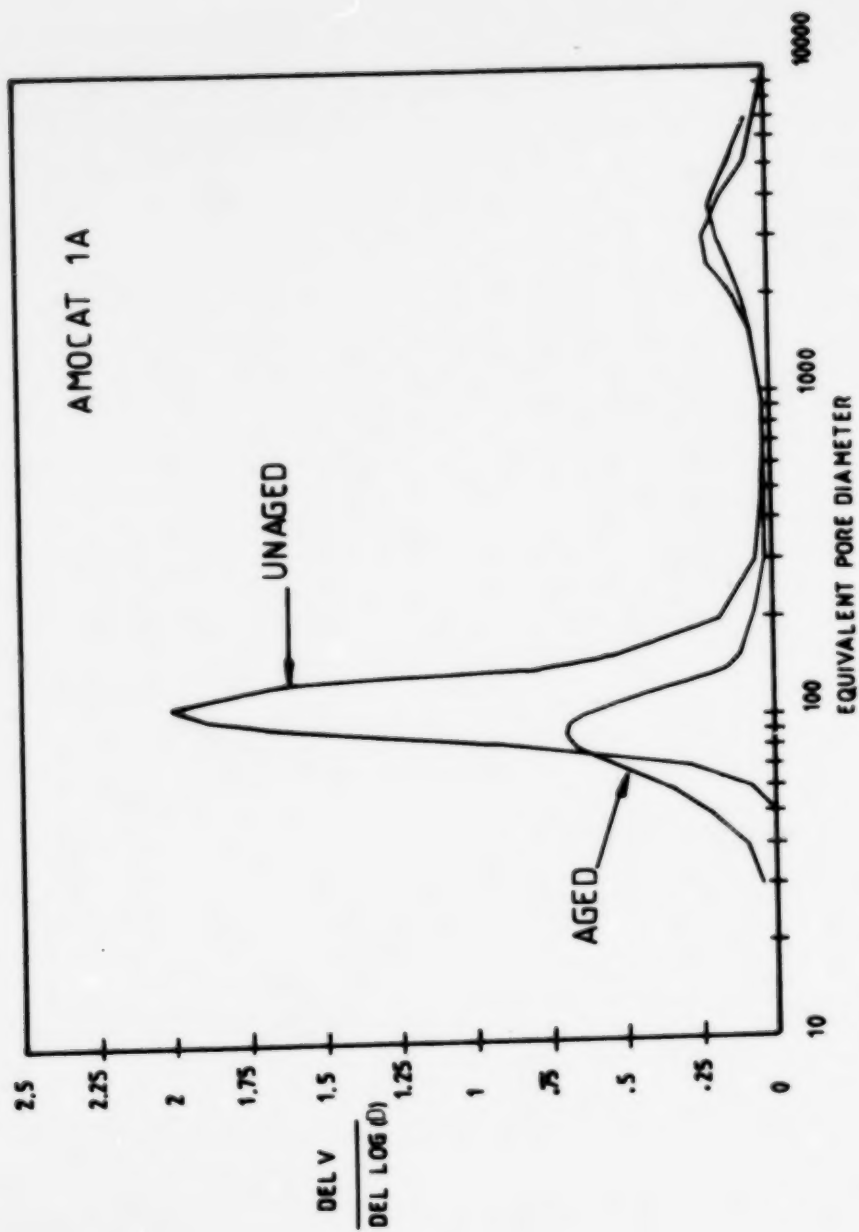


Figure 11.3 Transcribed DOE pore structure, catalyst RET 50570



PORE SIZE DISTRIBUTION FOR AGED AND UNAGED CATALYST

Figure 11.4 Transcribed DOE pore structure, catalyst AMOCAT 1A

The packed columns are preconditioned by heating in a flow of carrier gas at 250°C for 2 hours. The diffusion and adsorption characteristics of He, N₂, Ar, Kr, and CO₂ are considered for some or all of the catalysts. For most gases, pulses are taken at 3-4 temperatures in the range of 50-150°C and at 4-6 velocities ranging from 5-30 cm/sec. The column characteristics are described in Table 11.3. Bed voidage is calculated from known column volume, packing weight and apparent catalyst density.

TABLE 11.3 COLUMN CHARACTERISTICS FOR THE SIX CATALYSTS

Type	L	d	d _p	E	Pulses
	cm	cm	cm		
Fresh					
RET 50570	48	.635	.102	.416	He, N ₂ , Ar, CO ₂
AMOCAT 1A	48	.635	.140	.521	He, N ₂ , Ar, CO ₂
SHELL 324	48	.635	.082	.422	He, N ₂ , Ar, Kr, CO ₂
Fouled					
RET 50570	48	.635	.102	.433	He, N ₂ , Ar, CO ₂
AMOCAT 1A	48	.635	.140	.475	He, N ₂ , Ar, CO ₂
SHELL 324	48	.635	.082	.401	He, N ₂ , Ar, Kr, CO ₂

The output signal pulse is normalized and characterized by calculation of the first moment (eq. 11-18), the second central moment (eq. 11-19), the first ten Fourier coefficients (eqs. 11-20 to 11-22) and the amplitude ratios (eq. 11-25). The rapidly oscillating integrand of equations 11-20 to 11-22 may create errors in the calculation of higher harmonic components using the chosen integration scheme, Simpson's rule. However, it has been determined that the density of points defining the pulse shape is adequate for accurate calculation of the first ten harmonics.

The parameters contained in the previously described dispersion model, eqs. 11-1 to 11-18, are calculated by minimizing the objective

function constructed from the variance of the experimental and model amplitude ratios, eq. 11-23. A pattern search optimization routine is utilized for this purpose. In some cases nearly Gaussian peaks emerged for a wide range of velocities tested. The difficulties encountered due to the occurrence of local minima for symmetric peaks is discussed by Boersma-Klein and Moulijn (17). In order to surmount this difficulty, the use of the HETP method as described by van Deemter (24) was considered. The results from HETP analysis were used to derive starting points for the optimization routine based on amplitude ratios, thus allowing discrimination between local minima. In order to reduce the degrees of freedom in the optimization routine, the mass transfer coefficient, k_f , was calculated from the Ranz equation (25). In most cases the contribution of particle-to-gas mass transfer is minimal.

11.6 RESULTS

Test runs were made to compare the values of pellet porosity obtained from the pulse dispersion technique with those obtained from mercury penetration methods. For these runs, a combination of He tracer/ N_2 carrier is chosen. Helium is assumed to be nonadsorbing at the temperature range considered. By application of equation 11-14, the pulse-derived value of pellet porosity, β^* , is calculated as:

$$\beta^* = ((\mu_1')_C V/L - 1) E/(1-E) \quad (11-26)$$

where $(\mu_1')_C$ is the extra column volume corrected first absolute moment. Values of β^* are compared with mercury penetration-derived porosities, β , in Table 11.4. All of the pulse-calculated values of porosity are within about 5% of the mercury penetration values with the exception of the fouled shell catalyst. Scrutiny of the pore distribution for the fouled Shell catalyst reveals that a potentially significant portion of the small pore volume resides in the region undetected by the penetration procedure. A rough extrapolation of the distribution data indicates that the pulse-derived porosity is indeed consistent.

TABLE 11.4 COMPARISON OF MERCURY PENETRATION AND PULSE-DERIVED POROSITY

Type	Velocity cm/sec	β	β^*
Fresh			
RET 50570	18.00/7.33	.710	.703/.727
AMOCAT 1A	15.16/6.03	.717	.704/.700
SHELL 324 m	16.73/7.38	.600	.602/.582
Fouled			
RET 50570	15.21/7.23	.510	.517/.544
AMOCAT 1A	15.58/6.50	.527	.500/.525
SHELL 324 m	16.08/9.45	.25*	.317/.319

In the case of the fouled pellets, there is evidence that suggests that the local porosity is a function of radial position. By extension of equations 11-1 to 11-8 to include multiple zones of differing effective diffusivity and local porosity for a nonadsorbable tracer, it may be shown that β^* represents a volume-averaged porosity. Thus, β^* is in theory identical to β derived from mercury penetration methods regardless of gradients in local pore structure.

11.7 EFFECTIVE DIFFUSIVITY

In each of the three catalyst systems studied, fouling resulted in a substantial reduction in the calculated effective diffusivity as determined by pulse dispersion analysis. The most striking of these reductions (30-fold) is observed for the unimodal Shell catalyst. The two bimodal catalysts show much less pronounced decrease in the effective diffusivity due to fouling. A 3-fold and 5-fold reduction is noted for the RET 50570 and the AMOCAT 1A, respectively.

The calculated values of the effective diffusivities of CO_2 and He at 50°C for the six catalysts are shown in Table 11.5. The pulse-derived diffusivities are compared to those predicted by the Random Pore Model of Wakao and Smith (26). The method for calculating the theoretical diffusivity is shown below:

$$(D_e)_{th} = \beta_m^2 D_m + \beta_\mu (1 + 3\beta_m) D_\mu / (1 - \beta_m) \quad (11-27)$$

where,

$$1/D_m = 1/D_{AB} + 1/(D_k)_m \quad (11-28)$$

$$1/D_\mu = 1/D_{AB} + 1/(D_k)_\mu \quad (11-29)$$

$$(D_k)_m = 9.7 \times 10^{-5} \bar{r}_m (T_g/MW)^{1/2} \quad (11-30)$$

$$(D_k)_\mu = 9.7 \times 10^{-5} \bar{r}_\mu (T_g/MW)^{1/2} \quad (11-31)$$

where $\bar{r}$ is in Angstroms and T_g is in degrees Kelvin. β_m is taken to be the porosity of pores with diameters greater than 1000 angstroms. $\bar{r}_m$ is approximated as the peak of the macro pore distribution. $\bar{r}_\mu$ is calculated as follows:

$$\bar{r} = 2(V_g) \mu / Sg \quad (11-32)$$

TABLE 11.5 INTRAPELLET DIFFUSIVITIES: COMPARISON WITH RANDOM PORE MODEL

Type	$\bar{r}_\mu$	$\bar{r}_m$	β_μ	β_m	D_e	$(D_e)_{th}$
	Angstroms				$\text{cm}^2/\text{sec} \times 10^3$ Helium/CO ₂	
Fresh						
RET 50570	62	850	.568	.142	40.1/13.9	34.5/11.8
AMOCAT 1A	60	1500	.638	.079	32.4/11.0	29.6/10.0
SHELL 324 m	42	--	.600	--	11.5/4.2	12.5/3.4
Fouled						
RET 50570	58	800	.368	.142	10.6/4.3	17.8/7.7
AMOCAT 1A	42	1750	.416	.110	5.0/2.43	13.0/5.8
SHELL 324 m	25	--	.320	--	.45/.15	2.16/.66

The values of effective diffusivity calculated from the pulse dispersion data were independent of the carrier gas velocity. For most cases, a maximum variation in D_e of 15% was observed for velocities ranging from 10-30 cm/sec. The dependence of D_e on molecular weight

of the tracer gas is found to be roughly proportional to $(MW)^{-1/2}$ as expected. The dependence of D_e on column temperature is consistent with expectations $(T_g^{1/2} - T_g^{3/2})$, although the data are scattered.

As seen from Table 11.5, the predicted values of D_e for fresh catalysts calculated from the Random Pore model agree quite well with those determined from pulse analysis for the fresh catalysts. A twofold, threefold, and fivefold discrepancy is observed for the fouled RET 50570, AMOCAT 1A and the Shell 324 m, respectively.

Using static diffusion methods, Kim and Smith (27) observed similar trends in the effective diffusivity in nickel-oxide pellets upon sintering. The Random Pore model accurately predicted the value of the diffusivities in the unsintered pellet but overestimated the diffusivity by a factor of 2-3 for the sintered pellet. This behavior suggests a possible parallel between sintering and fouling of porous solids.

The Random Pore model assumes that the pellet possesses a homogeneous pore structure, that is, porosity and pore dimensions remain constant throughout the radial coordinate. In the case of the fouled catalysts, it is not unlikely that a more heavily fouled layer exists near the external surface of the pellet. This theory is supported by evidence that the activity of the fouled catalyst is largely restored by fracturing the pellet, thus exposing a surface of lower diffusional resistance (28). The existence of a heavily fouled, low porosity, surface layer is perhaps sufficient to explain the departure of the Random Pore model predictions from those calculated by pulse dispersion. In order to illustrate the effect of a heavily fouled surface layer on the pulse dispersion of a nonadsorbable tracer, a simplified progressive fouling model is described.

11.8 PROGRESSIVE FOULING MODEL

A model is proposed to account for the fouling of a pellet in terms of a well-defined pellet surface layer. It is assumed that the local porosity of the unfouled (internal) region of the fouled pellet is identical to the average porosity of the unfouled pellet. The effect

of the fouled layer on pulse dispersion (second central moment) is accounted for using a two-zone pellet model such as that proposed by Chou and Hegedus (22). Figure 11.5 depicts the two-zone model. The pertinent model equations follow.

The mass balance for the intra-pellet unfouled layer is given by:

$$\frac{D_{e1}}{\beta_1} \left(\frac{\partial^2 C_1}{\partial r^2} + \frac{1}{r} \frac{\partial C_1}{\partial r} \right) = \frac{\partial C_1}{\partial t} \quad 0 < r < a \quad (11-33)$$

The mass balance for the intra-pellet fouled layer is given by:

$$\frac{D_{e2}}{\beta_2} \left(\frac{\partial^2 C_2}{\partial r^2} + \frac{1}{r} \frac{\partial C_2}{\partial r} \right) = \frac{\partial C_2}{\partial t} \quad a < r < R \quad (11-34)$$

The constraint on the net (average) porosity of the fouled pellet, β , is given as:

$$\beta_1 \left(\frac{a^2}{R^2} \right) + \beta_2 \left(\frac{R^2 - a^2}{R^2} \right) = \beta \quad (11-35)$$

where, $\beta_1 = (\beta)$ unfouled.

Equations (11-33) and (11-34) may be substituted into the general pulse dispersion model described in the previous section where it is now assumed that the tracer is non-adsorbable. Solution of this model for the intra-pellet diffusivity contribution to pulse dispersion gives:

$$\delta_i(\text{zoned}) = \frac{2L}{V} \left(\frac{-\varphi_i D_{e2}}{R^2} + \frac{2\beta_2}{R} \left(\frac{\psi_2 R}{2} - \frac{\beta_2 R^3}{16D_{e2}} \right) \right) \quad (11-36)$$

where,

$$\begin{aligned} \varphi_i = & \frac{2\beta_2 a}{D_{e2}} \left(\frac{\psi_2 a}{2} - \frac{a^2(\beta_2 - \beta_1)}{2D_{e2}} \left(\frac{a}{2} \ln \left(\frac{a}{R} \right) - \frac{a}{4} \right) - \frac{\beta_2 a^3}{16D_{e2}} \right) \\ & - \frac{2\beta_1 a}{D_{e2}} \left(\frac{\psi_1 a}{2} - \frac{\beta_1 a^3}{16D_{e1}} \right) \end{aligned} \quad (11-37)$$

$$\psi_1 = \frac{\beta_2(R^2 - a^2)}{4D_{e2}} + \frac{\beta_1 a^2}{4D_{e1}} + \frac{a^2(\beta_2 - \beta_1)}{2D_{e2}} \ln \left(\frac{a}{R} \right) \quad (11-38)$$

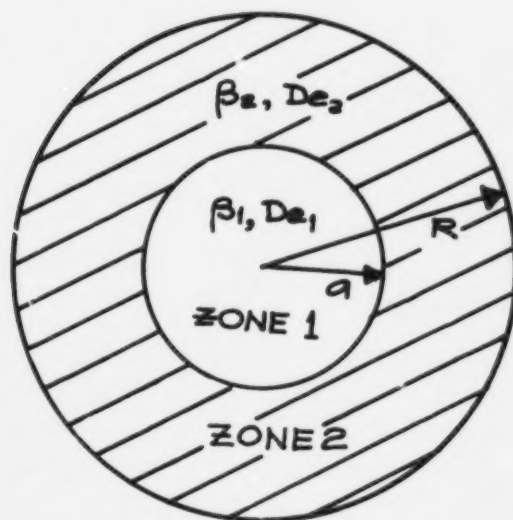


Figure 11.5 Schematic of progressive fouling zone model

and,

$$\psi_2 = \frac{\beta_2 R^2}{4D_{e2}} \quad (11-39)$$

For the case of a homogeneous pellet, $\beta_1 = \beta_2 = \beta$ and $D_{e1} = D_{e2} = D_e$, and the solution for δ_i reduces to the result of expression (A-17) as shown:

$$\delta_i = \frac{2L}{V} \left(\frac{\beta^2 R^2}{8D_e} \right) \quad (11-40)$$

From equations (11-38) to (11-41), it is evident that the intra-pellet dispersion contribution depends on the specific distribution of local porosity within the pellet.

Assuming cylindrical pores, the ratio of effective diffusivity in the homogeneously fouled catalyst to that in each zone of the progressively fouled catalyst is given by:

$$D_e/D_{e1} = (\beta/\beta_1)^{5/2} \quad (11-41)$$

$$D_e/D_{e2} = (\beta/\beta_2)^{5/2} \quad (11-42)$$

From equations (11-35) to (11-42) it is easily shown that for a given average extent of fouling (β), the ratio of intra-pellet dispersion in the zoned pellet to that in the homogeneous pellet, $\delta_i(\text{zoned})/\delta_i(\text{homo})$, depends only on the local porosity of the fouled zone, β_2 .

Figure 11.6 shows a plot of $\delta_i(\text{zoned})/\delta_i(\text{homo})$ versus β_2 for $\beta_1 = .5$ and $\beta = .3$. It is evident that, as the porosity of the fouled zone diminishes, the pulse dispersion increases compared to the case where the porosity (fouling) is evenly distributed. These results may partially explain the observation that the pulse-derived values of D_e are smaller than those predicted from the Random Pore model which assumes homogeneous radial properties. The most important conclusion that can be drawn from the simplified model presented above is that for equivalent pellet-averaged extents of fouling, process conditions that tend to restrict fouling to areas near the pellet surface are reflected in increased pulse dispersion compared to the case of evenly distributed

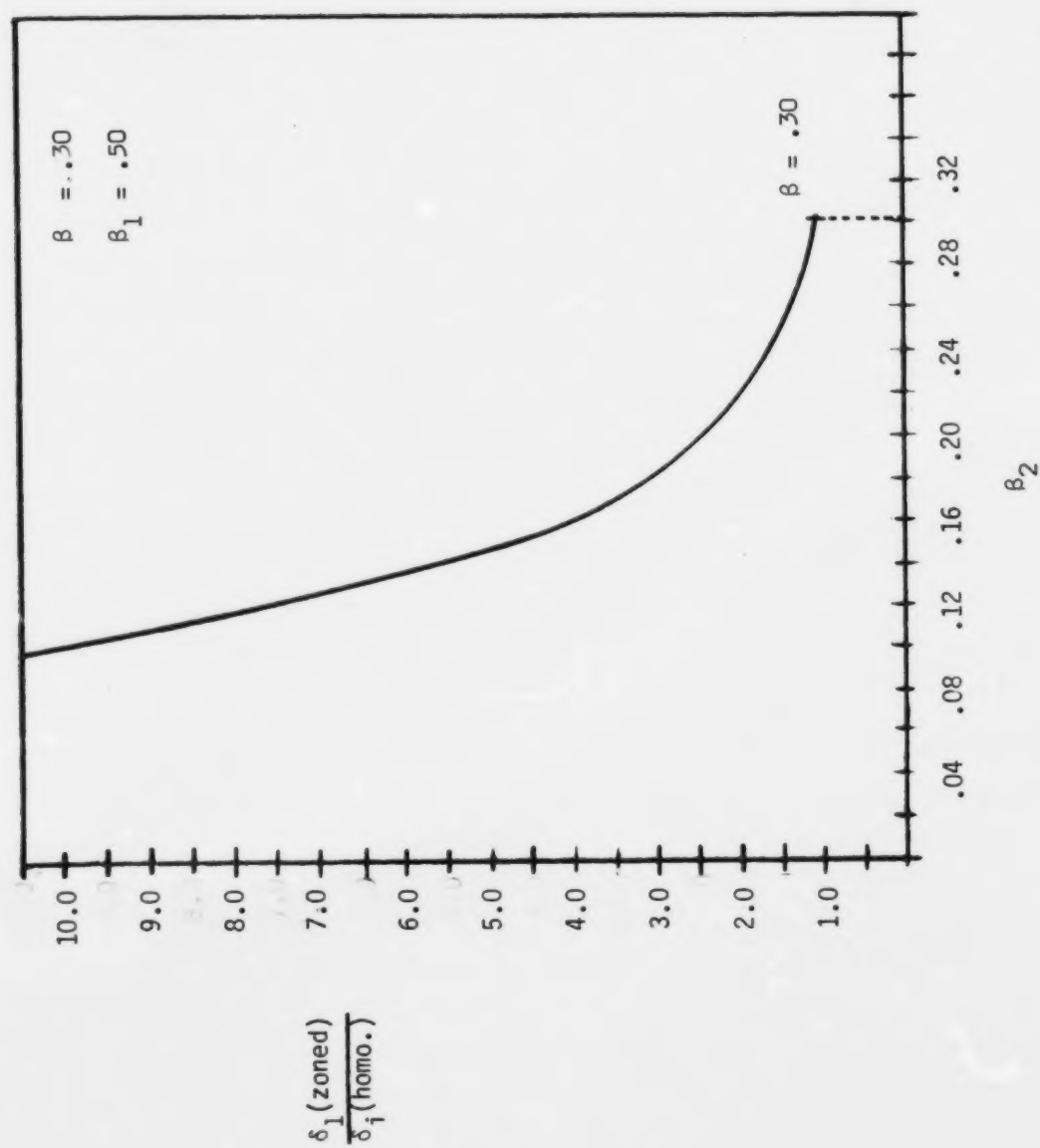


Figure 11.6 The effect of the fouled zone porosity on the intra-pellet dispersion contribution

fouling. This result suggests that pulse dispersion in fouled catalysts may provide qualitative insight into the nature and distribution of deposited matter within the pellet.

11.9 ADSORPTION

The functional dependence of the Henry's law adsorption constant, K_a , on $1/T_g$ is shown for various gases in Figures 11.7 to 11.9. The heats of adsorption calculated from the slopes of the curves are summarized in Table 11.6. The magnitude of the heat of the adsorption for CO_2 , Ar and N_2 are in the ranges expected for physical adsorption. The anomalous behavior of CO_2 adsorption will be discussed in the following section.

TABLE 11.6 HEAT OF ADSORPTION FOR CO_2 , Ar AND N_2 ON FRESH AND FOULED CATALYSTS

Type	Heat of Adsorption (kcal/gmole)		
	CO_2	Ar	N_2
<u>Fresh</u>			
RET 50570	6.2	2.3	2.5
AMOCAT 1A	6.9	2.4	3.3
SHELL 324 m	6.9	3.3	-
<u>Fouled</u>			
RET 50570	6.9	2.4	2.6
AMOCAT 1A	7.2	2.4	3.2
SHELL 324 m	7.2	3.1	3.3

The relative surface affinity for each catalyst system is summarized in Table 11.7. The relative surface affinity is defined as follows:

$$(K_a)_r = \frac{(K_a)_{\text{fouled}} / (S_g)_{\text{fouled}}}{(K_a)_{\text{fresh}} / (S_g)_{\text{fresh}}} \quad (11-43)$$

The data indicate that the adsorption of Argon per unit surface area is greater for the fouled catalyst compared to the fresh catalyst, while adsorption of N_2 is greater on the fresh catalyst. CO_2 is found to adsorb to a greater extent on the fouled nickel-containing catalysts

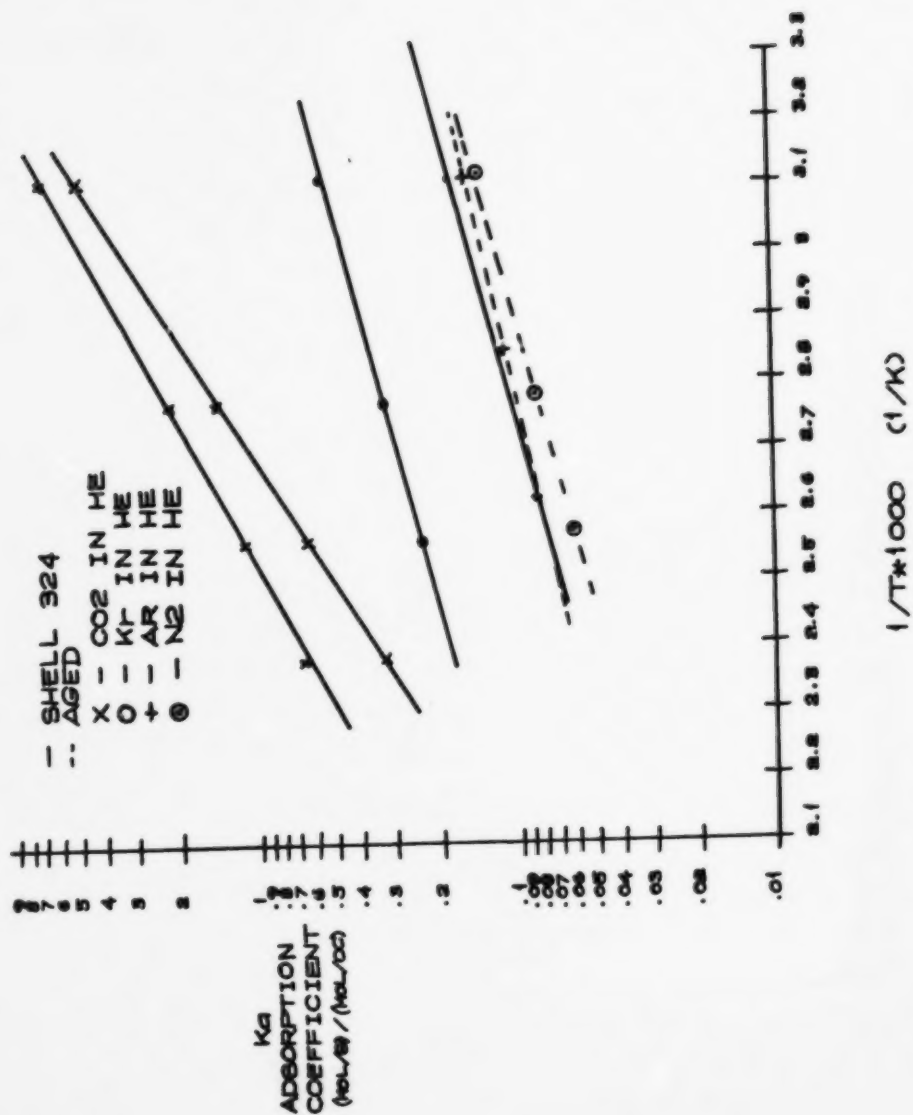


Figure 11.7 Dependence of K_a on T for Shell 324 catalyst

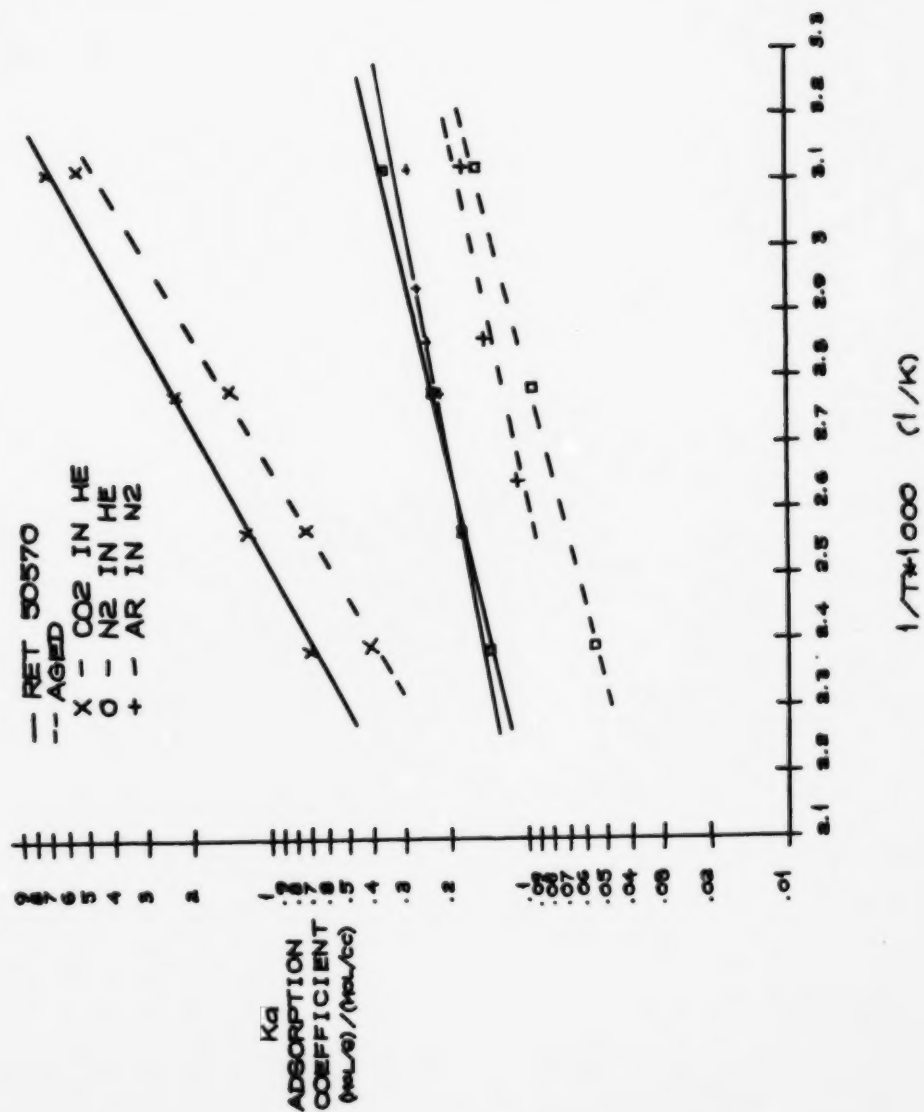


Figure 11.8 Dependence of K_a on T for RET 50570

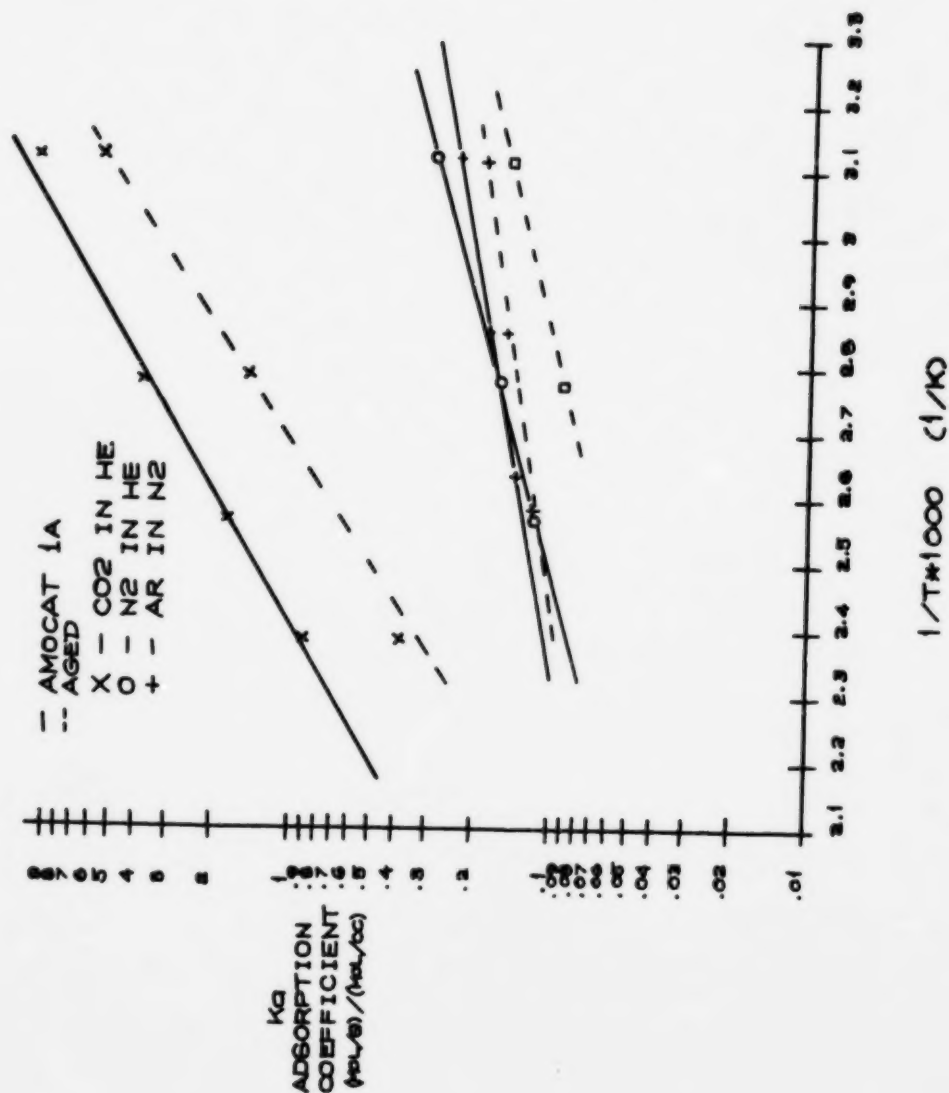


Figure 11.9 Dependence of K_a on T for AMOCAT 1A

compared to the fresh counterpart and to a lesser extent on the fouled cobalt-containing catalyst.

TABLE 11.7 RELATIVE SURFACE AFFINITY OF CO₂, Ar,
AND N₂ ON CATALYST SYSTEMS

Type	Relative Surface Affinity		
	CO ₂	Ar	N ₂
RET 50570 (Ni)	1.44	1.18	.86
SHELL 324 m (Ni)	1.32	1.37	.80
AMOCAT 1A (Co)	.75	1.19	.70

11.10 ADSORPTION OF CO₂

No combination of parameters contained in the single-size, adsorption model for a cylindrical pellet provided an adequate fit to the pulse shapes for CO₂. Typical best-fit variables resulted in an objective function value (equation 11-23) of the order 10^{-4} - 10^{-5} . While in other cases the best-fit objective function values were in the range of 10^{-6} to 10^{-8} . Furthermore, the best-fit variables gave substantially smaller effective diffusivities than could be justified from the given pore structure.

The difficulty arose from the inability of the single-site adsorption model to simulate the attenuated tail of the CO₂ pulse. In order to ensure that this tail was not simply an artifact of nonlinear adsorption, the concentration of CO₂ in the sample loop was progressively lowered down to the limits of sensitivity of the TC detector. No significant change in pulse shape or mean residence time was noted, indicative of linear adsorption. The tailing pulse shape suggested an apparent two-site adsorption process. One of the sites is characterized by a fast desorption step such as typically encountered in physical adsorption, while a second site possesses properties of a much slower desorption step. Due to the heterogeneous nature of the surfaces considered, it

is not too surprising that a more selective tracer such as CO_2 might exhibit such behavior.

The two-site model was applied to the CO_2 adsorption with extremely promising results. Improvement of the best-fit criterion of two orders of magnitude was observed compared to the single-site model. An example of the fits obtained for the two models for fresh AMOCAT 1A is shown in Figure 11.10.

The slow desorption site is characterized by an equilibrium constant, K_{a2} , of approximately 10% of the fast desorption site. The forward rate of adsorption on the minor sites is found to be a weak function of temperature. Both K_{a2} and k_r , the rate of desorption, exhibits an Arrhenius temperature dependence. The activation energy of desorption is nearly equal to the heat of adsorption, implying nonactivated adsorption. The temperature dependence of K_{a2} for the minor sites is depicted in Figure 11.11. The consistency of these trends with respect to the temperature dependence of K_{a2} indicates that the two-site model seems to have physical significance and that the improvement in the best-fit criterion is not simply an artifact of the increased degrees of freedom which the model possesses compared to the single-site case.

Transition state theory suggests that the velocity of adsorption, u_a , and desorption, u_d , may be calculated from the following expressions (32):

$$u_a = (\sigma_s P_g / (2\pi m k T_g))^{1/2} f(\theta_c) \exp(-E/RT_g) \quad (11-44)$$

$$u_d = K f'(\theta_c) \exp(-E'/RT_g) \quad (11-45)$$

where σ_s is an empirical sticking coefficient, $f(\theta_c)$ and $f'(\theta_c)$ are functions of the coverage of adsorbable sites, E is the activation energy for adsorption, and E' equals the sum of E and the heat of adsorption. Gangwall et al. (33) suggest that physical adsorption or nonactivated chemisorption occurs at a rate many orders of magnitude too fast for determination by pulse dispersion based on equations (11-44) and (11-45). However, other investigations (1) have presented results that indicate

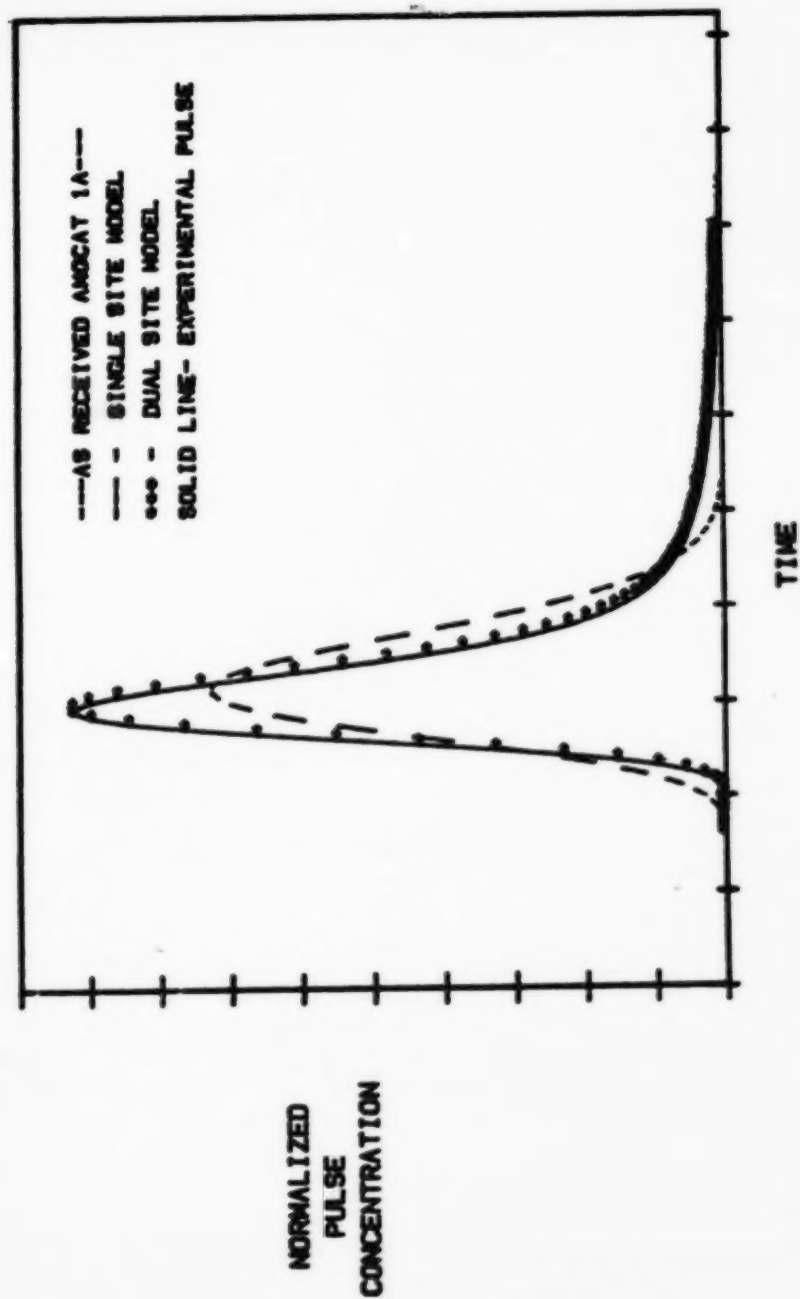


Figure 11.10 Normalized pulse concentration versus time: comparison of single site and dual site adsorption model

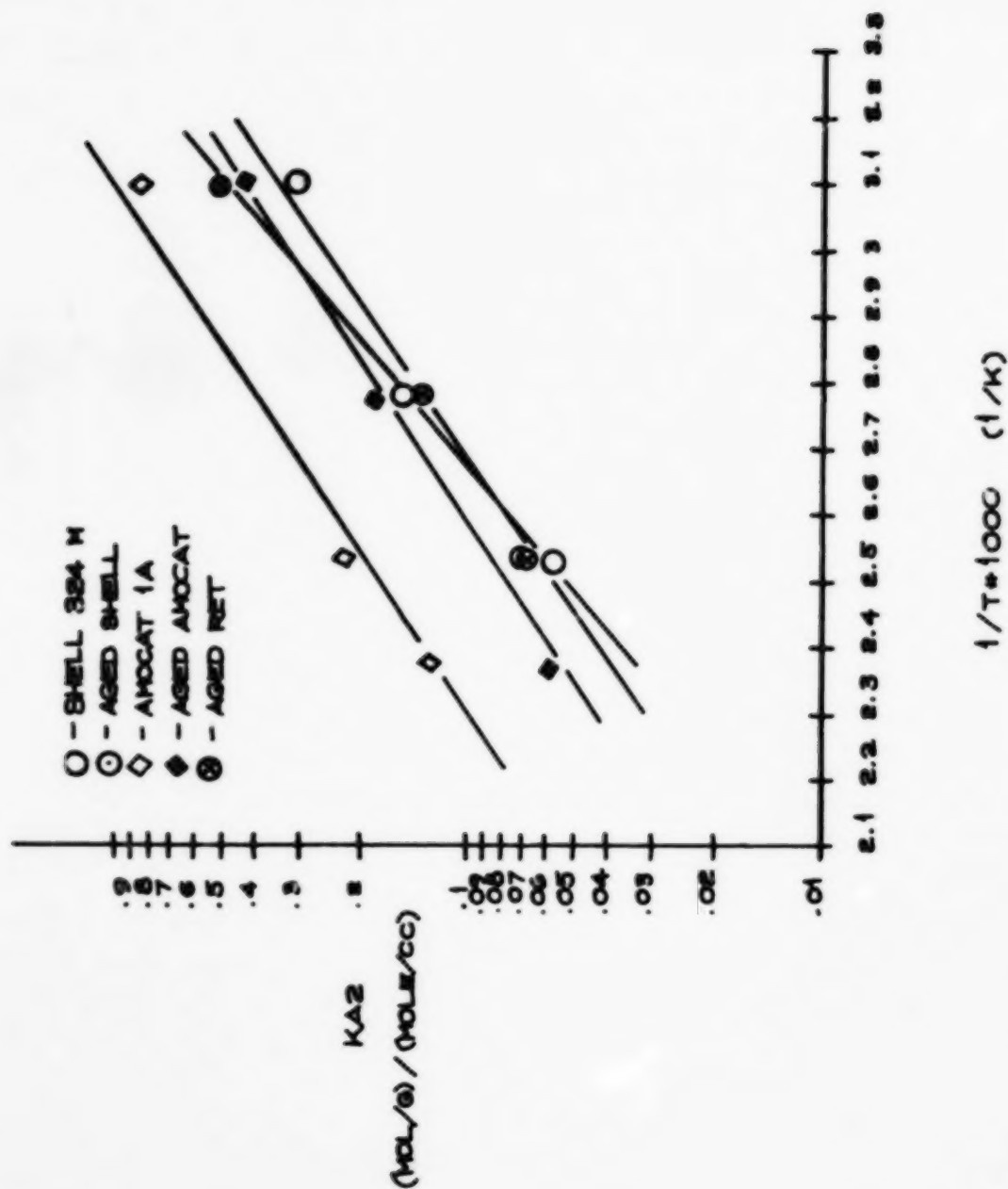


Figure 11.11 Temperature dependence of K_a for the "minority" sites

the rate of adsorption is many orders of magnitude smaller than those predicted from equations (11-39) and (11-40). It should be mentioned that the rate of desorption and adsorption measured for CO_2 on the minority sites using the dual site interpretation are a few orders of magnitude smaller than the values predicted from transition state theory.

CO_2 is known to chemisorb on metal oxides. Garner (34) and Ward (35) discuss the behavior of CO_2 adsorption on various oxides. Their results indicate that the adsorption of CO_2 is nonactivated. Heats of adsorption ranged from 13-23 kcal/mole and depended on surface coverage. The chemisorbed species was considered to be in the form of a carbonate complex. The heats of adsorption on the minority sites calculated using the dual site model are smaller than the heats reported above by a factor of two, suggesting physical adsorption. However, no definitive discrimination between physisorption and chemisorption has been made for this case.

11.11 CONCLUSIONS

A model has been developed that allows applying Fourier analysis to pulse dispersion of an adsorbable tracer in cylindrical pellets. This model extends the Kubin-Kucera treatment of diffusion and adsorption in a pellet to include the commonly encountered extrudite geometry which is found in many commercial catalysts.

Values of first absolute moments for pulses of a nonadsorbable tracer (He) were determined in order to calculate the volume average porosity of fresh and fouled catalysts. These values were found to be consistent with mercury penetration-derived values within 5%.

The results of pulse dispersion analysis on fresh and fouled HDS catalysts reveal that the diffusional resistances in the fouled catalyst increase substantially, compared to that in the fresh one. The reduction in the effective diffusivity of the fouled compared to the fresh catalyst is approximately an order of magnitude. The Random Pore model accurately predicts the effective diffusivity for fresh HDS catalysts containing unimodal or bimodal pore distributions. However, the effective

diffusivities in fouled HDS catalysts are two- to fivefold lower than those predicted from the Random Pore model assuming that the local porosity is constant throughout the radial coordinate of the pellet.

A simplified model is presented which accounts for pulse dispersion in a pellet with radially nonuniform properties. The deviations between the measured and predicted values of effective diffusivity in fouled HDS catalysts may perhaps be interpreted in terms of increased pulse dispersion due to pore mouth fouling.

The relative adsorption affinities of N_2 , Ar and CO_2 are calculated for the three catalyst systems. The relative adsorption affinity is found to be in the range of .7 to .86 for N_2 and 1.18 to 1.36 for Ar. The relative adsorption affinity for CO_2 , a more selective adsorber, is shown to depend strongly on the particular chemical structure of the adsorbing surface. A relative adsorption affinity value of .75 is noted for the cobalt-containing catalyst and 1.32-1.44 for the nickel-containing one. These results suggest a potential correlation between K_a and physical surface area for less selective adsorbers, while K_a for more selective adsorbers may correlate with the chemical nature of the surface. An apparent two-site mechanism was presented to describe the adsorption behavior of CO_2 and HDS catalysts. Based on this interpretation, a slow desorption step was calculated for the minority adsorption sites. The minority sites represent 10% of the total adsorption sites based on the relative magnitude of K_a for the two sites. The specific chemical identity of these sites has not been identified.

The results of this study indicate the potential of the pulse dispersion technique as a tool for probing the physical and chemical transformations of porous solids such as that which occurs during the fouling of HDS catalysts used in coal liquefaction or coal liquid upgrading service.

11.12 REFERENCES

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11.13 APPENDIX A

A model was described for the dispersion of an adsorbable tracer in a packed column containing porous cylindrical pellets with a heterogeneous surface. Solution of the model in the Fourier domain gives the following result:

$$\bar{C}(iw) = \exp \left(P - \left(P^2 + \frac{i w E L}{D_a} (1 + h(iw)) \right)^{1/2} \right) \quad (A1)$$

where P and $h(iw)$ are defined in equations (11-10) and (11-11), respectively. The solution is separated into real and imaginary parts to give:

$$\begin{aligned} \bar{C}(iw) = \exp \left(P - \sqrt{\sigma} \cos(\psi/2) \right) \times & \left(\cos(\sqrt{\sigma} \sin(\psi/2)) \right. \\ & \left. + i \sin(\sqrt{\sigma} \sin(\psi/2)) \right) \end{aligned} \quad (A2)$$

where,

$$\sigma = (\alpha^2 + \eta^2)^{1/2} \quad (A3)$$

$$\psi = \text{ArcTan}(\eta/\alpha) \quad (A4)$$

$$\alpha = P^2 - (L^2 w E / D_a) \gamma \quad (A5)$$

$$\eta = (1 + X)(L^2 w E / D_a) \quad (A6)$$

$$X = -S_v k_f (\sigma_1 \varphi + \sigma_2 \gamma) / (\varphi^2 + \gamma^2) \quad (A7)$$

$$\gamma = -S_v k_f (1/w + (\sigma_2 \varphi - \sigma_1 \gamma) / (\varphi^2 + \gamma^2)) \quad (A8)$$

$$\varphi = -((D_e w \sqrt{\rho} / k_f R)(\theta \cos(q/2) + \mu \sin(q/2)) + w \sigma_2) \quad (A9)$$

$$\gamma = (D_e w \sqrt{\rho} / k_f R)(\mu \cos(q/2) + \theta \sin(q/2)) + w \sigma_1 \quad (A10)$$

$$\mu = (\sqrt{\rho}/2)(\sigma_3 \cos(q/2) - \sigma_4 \sin(q/2)) \quad (A11)$$

$$\theta = (\sqrt{\rho}/2)(\sigma_4 \cos(q/2) + \sigma_3 \sin(q/2)) \quad (A12)$$

$$\sigma_1 = \sum_{k=0}^n (\rho/4)^k \cos(kq) / (k!)^2 \quad (A13)$$

$$\sigma_2 = \sum_{k=0}^n (\rho/4)^k \sin(kq)/(k!)^2 \quad (A14)$$

$$\sigma_3 = \sum_{k=0}^n (\rho/4)^k \cos(kq)/(k!(k+1)!) \quad (A15)$$

$$\sigma_4 = \sum_{k=0}^n (\rho/4)^k \sin(kq)/k!(k+1)!) \quad (A16)$$

$$q = \text{ArcTan}(\tau/\zeta) \quad (A17)$$

$$\rho = (\tau^2 + \zeta^2)^{1/2} \quad (A18)$$

$$\begin{aligned} \zeta = & (w^2 R^2 \rho_p / D_e) ((k_{a1} / ((k_{a1} / K_{a1})^2 + w^2)) \\ & + k_{a2} / ((k_{a2} / K_{a2})^2 + w^2)) \end{aligned} \quad (A19)$$

$$\begin{aligned} \tau = & (w R^2 B / D_e) (1 + \frac{\rho_p}{B} ((k_{a1}^2 / K_{a1}) / ((k_{a1} / K_{a1})^2 + w^2) \\ & + (k_{a2}^2 / K_{a2}) / ((k_{a2} / K_{a2})^2 + w^2))) \end{aligned} \quad (A20)$$

The Fourier coefficients are given by:

$$a_n = (1/T \exp(P - \sqrt{\sigma} \cos(\psi/2)) \sin(\sqrt{\sigma} \sin(\psi/2)) \quad (A21)$$

$$b_n = (1/T \exp(P - \sqrt{\sigma} \cos(\psi/2)) \cos(\sqrt{\sigma} \sin(\psi/2)) \quad (A22)$$

The amplitude ratio is:

$$A_n = \exp(P - \sqrt{\sigma} \cos(\psi/2)) \quad (A23)$$

For the range of variables encountered in this study, the infinite series in equations (A13)-(A16) were found to converge to six significant digits with less than 20 terms. In many cases convergence occurred with less than three or four terms.

11.14 NOTATION

a	= coordinate of the leading edge of the fouled zone
A_n, A_n^*	= theoretical and experimental amplitude ratios defined by equations (11-24) and (11-25)
a_n, b_n, a_n^*, b_n^*	= theoretical and experimental Fourier coefficients defined by equations (11-20)-(11-22) and (A21)-(A22)
$C(t)$	= concentration of tracer in inter-pellet volume; mole/cc
$C^*(t)$	= normalized residence time distribution of experimental pulse
$\bar{C}(iw)$	= Fourier transform of $C(t)$, equation (11-9)
$C_i(t)$	= concentration of tracer in intra-pellet pore volume; mole/cc
C_{a1}, C_{a2}	= concentration of adsorbed gas per unit weight of absorbant; mole/g
C_1	= concentration in pore volume of unfouled zone; mole/cc
C_2	= concentration in pore volume of fouled zone; mole/cc
d	= column diameter; cm
d_p	= diameter of cylindrical pellet; cm
D_a	= effective axial dispersion coefficient; cm^2/sec
D_{AB}	= binary gas diffusivity; cm^2/sec
D_e	= effective intra-pellet diffusivity; cm^2/sec
D_{e1}	= effective diffusivity in the unfouled zone; cm^2/sec
D_{e2}	= effective diffusivity in the fouled zone; cm^2/sec
$(D_e)_{th}$	= effective diffusivity predicted by Random Pore model, equation (11-26); cm^2/sec
$(D_k)_m$	= Knudsen contribution in macropore; cm^2/sec
$(D_k)_\mu$	= Knudsen contribution in micropore; cm^2/sec
D_m	= diffusivity in macropore; cm^2/sec

D_{μ}	= diffusivity in micropore; cm^2/sec
E	= bed voidage
F	= value of objective function defined by equation (11-23)
k_{a1}, k_{a2}	= adsorption rate constant defined by equation (11-3), (11-4); cc/gsec
K_{a1}, K_{a2}	= adsorption equilibrium constant; cc/g
k_f	= mass transfer coefficient defined by equation (11-5); cm/sec
I_0	= zero modified Bessel Function
I_1	= first modified Bessel Function
P	= $(VEL/2D_a)$, equation (11-10).
q	= defined by equation (A17)
r	= coordinate in cylindrical pellet; cm
$\bar{r}_m$	= average macropore radius; Angstroms
$\bar{r}_{\mu}$	= average micropore radius defined as $2V_g/S_g$; Angstroms
$(\bar{r}_{\mu})_1$	= average micropore radius in unfouled zone
$(\bar{r}_{\mu})_2$	= average micropore radius in fouled zone
R	= radius of cylindrical pellet; cm
S	= surface area per gram of pellet
$(V_g)_{\mu}$	= pore volume per gram of pellet (micropore only)
t	= time; sec
T	= period of pulse; sec
T_g	= carrier gas temperature
V	= Interstitial fluid velocity; cm/sec
w	= frequency defined by $n \pi/T; \text{sec}^{-1}$
X	= defined by equation (A7)
Y	= defined by equation (A8)
Z	= axial coordinate of column

A.15 GREEK NOTATION

α	= defined by equation (A5)
β	= pellet porosity
β_m	= porosity attributed to macropores
β_μ	= porosity attributed to micropores ($<1000 \text{ \AA}$)
β^*	= pulse-determined porosity
β_1	= local porosity of unfouled zone
β_2	= local porosity of fouled zone
$\delta(t)$	= Kronecker delta function
δ_o	= defined by equation (11-16)
δ_1	= defined by equation (11-17)
$\delta_i(\text{zoned})$	= effective diffusivity contribution to pulse dispersion in zoned pellet, given by equation (11-36)
$\delta_i(\text{homo})$	= effective diffusivity contribution to pulse dispersion in homogeneous pellet, given by equation (11-40)
λ	= defined by equation (11-13)
η	= defined by equation (A6)
ψ	= defined by equation (A4)
ψ_1	= defined by equation (11-38)
ψ_2	= defined by equation (11-39)
φ	= defined by equation (A9)
φ_i	= defined by equation (11-37)
ρ	= defined by equation (A18)
ρ_p	= apparent pellet density; g/cc
θ	= defined by equation (A12)
σ	= defined by equation (A3)
$\sigma_1, \sigma_2, \sigma_3, \sigma_4$	= defined by equations (A13)-(A16)

μ	= defined by equation (A11)
μ_1^i	= first absolute moment, defined by equation (11-19)
μ_2	= second central moment, defined by equation (11-13)
τ	= defined by equation (A20)
ζ	= defined by equation (A19)
γ	= defined by equation (A10)
$(\mu_1^i)_c$	= corrected first absolute moment